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(54)【発明の名称】 アルカリ蓄電池用正極活物質及びその製造方法

(57)【要約】

【課題】 活物質粒子相互間の導電性を少ない量のコバルト化合物でもって効果的に向上させ、かつ過放電時においても母粒子表面近傍のコバルト化合物が水酸化ニッケル母粒子内部へ拡散することのないアルカリ蓄電池用正極活物質、及びそのような正極活物質の製造方法を提供することを目的とする。

【解決手段】 少なくとも水酸化ニッケルと、コバルト化合物とを含有する固溶体粒子を必須構成要素とするアルカリ蓄電池用正極活物質において、前記固溶体粒子が、粒子表層に高く粒子中心部に向かって減少するコバルト濃度勾配を有することを特徴とする。

【特許請求の範囲】

【請求項1】 少なくとも水酸化ニッケルと、コバルト化合物とを含有する固溶体粒子を必須構成要素とするアルカリ蓄電池用正極活物質であって、前記固溶体粒子は、粒子表層に高く粒子中心部に向かって減少するコバルト濃度勾配を有することを特徴とするアルカリ蓄電池用正極活物質。

【請求項2】 前記固溶体粒子は、更に、粒子表層のコバルト濃度と同等以上のコバルト濃度を有する水酸化コバルト被覆層が粒子表面に形成されたものである、ことを特徴とする請求項1記載のアルカリ蓄電池用正極活物質。

【請求項3】 前記水酸化コバルト被覆層中の水酸化コバルトは、被覆層の形成された固溶体粒子をアルカリと酸素の共存下で加熱処理することによって、2価を超えるコバルト化合物とされていることを特徴とする請求項2記載のアルカリ蓄電池用正極活物質。

【請求項4】 前記アルカリ蓄電池用正極活物質は、前記固溶体粒子と、前記固溶体粒子表層のコバルト濃度と同等以上のコバルト濃度を有する水酸化コバルト含有粉末とを含むことを特徴とする請求項1記載のアルカリ蓄電池用正極活物質。

【請求項5】 前記固溶体粒子は、更に、亜鉛化合物、カドミウム化合物、マグネシウム化合物、マンガン化合物からなる群より選択される1種以上の化合物を含有する、ことを特徴とする請求項1ないし請求項4記載のアルカリ蓄電池用正極活物質。

【請求項6】 少なくとも水酸化ニッケルとコバルト化合物を含有してなるアルカリ蓄電池用固溶体活物質粒子の製造方法において、前記アルカリ蓄電池用固溶体活物質粒子の製造方法は、攪拌下ニッケル塩溶液に対し、コバルト塩添加量が連続的または段階的に増加するようにコバルト塩溶液を注加し、これと同時に並行的にアルカリ溶液を注加して反応溶液pHを所定値に維持することにより、粒子中心部で低く粒子表層に高いコバルト濃度勾配を有するニッケル・コバルト固溶体粒子を作製する固溶体粒子作製工程を備えることを特徴とするアルカリ蓄電池用固溶体活物質粒子の製造方法。

【請求項7】 前記固溶体粒子作製工程において、反応溶液中にアンモニアを存在させることを特徴とする請求項6記載のアルカリ蓄電池用固溶体活物質粒子の製造方法。

【請求項8】 前記ニッケル・コバルト固溶体粒子を、少なくともコバルト塩を溶解したコバルト塩溶液に攪拌分散し、この攪拌分散液にアルカリ溶液を注加し分散液pHを所定値に調整することによりコバルト化合物を析出させ、前記ニッケル・コバルト固溶体粒子の表面に水酸化コバルト被覆層を形成する被覆層形成工程を更に備える、ことを特徴とする請求項6ないし請求項7記載の

アルカリ蓄電池用固溶体活物質粒子の製造方法。

【請求項9】 更に、前記被覆層形成工程で作製した被覆固溶体粒子にアルカリ金属溶液を含浸させた後、酸素存在下で熱処理するアルカリ熱処理工程を備える、ことを特徴とする請求項8記載のアルカリ蓄電池用固溶体活物質粒子の製造方法。

【請求項10】 前記アルカリ金属溶液が、水酸化カリウム溶液であることを特徴とする請求項9記載のアルカリ蓄電池用固溶体活物質粒子の製造方法。

【請求項11】 前記熱処理の温度が、40～100℃であることを特徴とする請求項9ないし請求項10記載のアルカリ蓄電池用固溶体活物質粒子の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明はアルカリ蓄電池用の正極活物質に関し、詳しくは水酸化ニッケルとコバルト化合物とで固溶体粒子となした水酸化ニッケル活物質の改良に関する。

【0002】

【従来の技術】アルカリ蓄電池用ニッケル正極の製法には、ニッケル粉末を焼結した焼結式基板に活物質を充填するいわゆる焼結式と、ニッケル繊維焼結多孔体や発泡ニッケル多孔体などの高多孔度のニッケル多孔体にペースト状の活物質を充填するいわゆるペースト式とがある。しかし、焼結式は、活物質の充填作業が煩雑であり、また基板の高多孔度化に限界があるため、電極の高エネルギー密度化を図り難いという欠点がある。このため、近年では、電池の高エネルギー密度化、低価格化の要請に応えるべく、高多孔度ニッケル体を用いたペースト式のニッケル正極が主流になりつつある。

【0003】しかしながら、ペースト式は多孔体への高密度充填が可能であるものの、集電体として機能する多孔体の細孔径が大きいために、多孔体と活物質との電気的接触が不十分となり、集電効率が悪いという欠点がある。このため、高密度に充填した活物質の発電能力を十分に引出し得ないという問題がある。

【0004】そこで、従来よりこのようなペースト式の欠点を改善することを目的とし、①水酸化ニッケルと水酸化カドミウム又は水酸化コバルトを含む固溶体活物質粉末の表面に水酸化コバルトの被覆層を形成する技術（特開昭62-222566号公報）や、②水酸化ニッケルの表面部に水酸化ニッケルと水酸化コバルトの固溶体を形成する技術（特開平3-62457号公報）、更には前記特開昭62-222566号公報に記載の技術を一層改良した技術として、③水酸化ニッケル表面に形成されたコバルト化合物を含む被覆層の上に親水性有機物膜を施す技術（特開平5-151962号公報）などが提案されている。これらの技術を適用した場合、活物質粒子相互間における導電性が向上するため、ニッケル正極の性能を向上させることができる。

【0005】

【発明が解決しようとする課題】ところが、上記の技術では、次のような問題点が解決できていない。即ち、水酸化ニッケル粒子表面に水酸化コバルトを配した場合、この水酸化コバルトが活物質粒子相互間の導電性を向上させるが、粒子表面の水酸化コバルトは、過放電時に水酸化ニッケルの内部に拡散し、粒子表面の水酸化コバルト量が減少するという現象が生じる。このため、活物質粒子の導電性が低下し、その利用率が低下し、特に過放電時において十分な電池容量が取り出せなくなるという問題がある。しかし、前記拡散を見込んで予め多量の水酸化コバルトを粒子表面又は活物質全体に配する方法では、水酸化ニッケル量（活物質本体の量）の相対的減少を招くため、エネルギー密度を十分に高めることができない。

【0006】また、前記③の技術は、被覆層の上に親水性有機物膜を施すことによりコバルト種が電解液中へ散逸するのを物理的に防止しようとする技術であるので、この技術でも母粒子内部に拡散する現象を抑制できない。

【0007】本発明は、前記従来技術における問題点を解決するためになされたものであり、活物質粒子相互間の導電性を少ない量のコバルト化合物でもって効果的に向上させ、かつ過放電時においても母粒子表面近傍のコバルト化合物が水酸化ニッケル母粒子内部へ拡散することのないアルカリ蓄電池用正極活物質、及びそのようなアルカリ蓄電池用正極活物質の製造方法を提供することを目的とする。

【0008】

【課題を解決するための手段】上記目的を達成するために、本発明は次の特徴を有している。請求項1記載の発明は、少なくとも水酸化ニッケルと、コバルト化合物とを含有する固溶体粒子を必須構成要素とするアルカリ蓄電池用正極活物質であって、前記固溶体粒子は、粒子表面に高く粒子中心部に向かって減少するコバルト濃度勾配を有することを特徴とする。

【0009】請求項2記載の発明は、請求項1記載のアルカリ蓄電池用正極活物質において、前記固溶体粒子の表面に粒子表面のコバルト濃度と同等以上のコバルト濃度を有する水酸化コバルト被覆層が形成されていることを特徴とする。

【0010】請求項3記載の発明は、前記水酸化コバルト被覆層中の水酸化コバルトが、被覆層の形成された固溶体粒子をアルカリと酸素の共存下で加熱処理することによって、2価を超えるコバルト化合物としてあることを特徴とする請求項2記載のアルカリ蓄電池用正極活物質。

【0011】請求項4記載の発明は、請求項1記載のアルカリ蓄電池用正極活物質が、前記固溶体粒子と、前記固溶体粒子表面のコバルト濃度と同等以上のコバルト濃

度を有する水酸化コバルト含有粉末とを含むことを特徴とする。

【0012】請求項5記載の発明は、請求項1ないし請求項4記載のアルカリ蓄電池用正極活物質において、前記固溶体粒子が、更に亜鉛化合物、カドミウム化合物、マグネシウム化合物、マンガン化合物からなる群より選択される1種以上の化合物を含有することを特徴とする。

【0013】請求項6記載の発明は、攪拌下ニッケル塩溶液に対し、コバルト塩添加量が連続的または段階的に増加するようにコバルト塩溶液を注加し、これと同時に並行的にアルカリ溶液を注加して反応溶液pHを所定値に維持することにより、粒子中心部で低く粒子表面に高いコバルト濃度勾配を有するニッケル・コバルト固溶体粒子を作製する固溶体粒子作製工程を備えるアルカリ蓄電池用固溶体活物質粒子の製造方法であることを特徴とする。

【0014】請求項7記載の発明は、請求項6記載のアルカリ蓄電池用固溶体活物質粒子の製造方法の固溶体粒子作製工程において、反応溶液中にアンモニアを存在させることを特徴とする。

【0015】請求項8記載の発明は、請求項6ないし請求項7記載のアルカリ蓄電池用固溶体活物質粒子の製造方法において、更に、前記ニッケル・コバルト固溶体粒子を、少なくともコバルト塩を溶解したコバルト塩溶液に攪拌分散し、この攪拌分散液にアルカリ溶液を注加し分散液pHを所定値に調整することによりコバルト化合物を析出させ、前記ニッケル・コバルト固溶体粒子の表面に水酸化コバルト被覆層を形成する被覆層形成工程を備えることを特徴とする。

【0016】請求項9記載の発明は、請求項8記載のアルカリ蓄電池用固溶体活物質粒子の製造方法において、更に、前記被覆層形成工程で作製した被覆固溶体粒子にアルカリ金属溶液を含浸させた後、酸素存在下で熱処理するアルカリ熱処理工程を備えることを特徴とする。

【0017】請求項10記載の発明は、請求項9記載のアルカリ蓄電池用固溶体活物質粒子の製造方法において、前記アルカリ金属溶液が、水酸化カリウム溶液であることを特徴とする。

【0018】請求項11記載の発明は、請求項9ないし請求項10記載のアルカリ蓄電池用固溶体活物質粒子の製造方法において、前記熱処理の温度が、40～100℃であることを特徴とする。

【0019】

【実施の形態】以下、本発明にかかるニッケル固溶体活物質粒子の作製方法およびこの固溶体活物質粒子を用いた正極の製造方法を説明し、その後この正極を組み込んだ電池により各種固溶体活物質粒子の電気化学的特性を説明することにより、本発明の実施の形態を明らかにする。

【0020】〔各種固溶体活物質粒子の作製〕

(本発明活物質粒子A₀の作製) 先ず、固溶体粒子の全重量を100とすると、亜鉛とコバルトの金属元素重量分率がそれぞれ0.5重量%、2重量%となるように、硫酸ニッケル水溶液(a液)、硫酸亜鉛水溶液(b液)、硫酸コバルト水溶液(c液)を用意した。次に前記a液とb液を攪拌混合し、このa・b液に対し、攪拌混合を続けながら、単位時間当たりの注加量が段階的又は連続的に増加するように注加量を制御しながら前記c液を添加するとともに、これと同時に並行的にa・b・c反応溶液のpHが所定値に維持されるようにアンモニア水および水酸化ナトリウム水溶液を徐々に添加した。これによりa・b・c反応溶液中に水酸化ニッケルを主成分とする活物質粒子が生成・析出するので、これを採取し、水洗・乾燥してニッケル・コバルト固溶体粒子を得た。以下、このニッケル・コバルト固溶体粒子を本発明活物質粒子A₀とする。

【0021】上記のようにa・b液に対するc液の注加量を段階的または連続的に増加する方法で各溶液を反応させた場合、ニッケル化合物、亜鉛化合物、コバルト化合物の3成分からなる固溶体粒子が得られ、この固溶体粒子は、コバルト化合物が粒子内部で低く粒子表面で高い濃度勾配(以下、Co濃度勾配という)をもって粒子内に分散したものとなる。

【0022】なお、上記a、b、cの各液の濃度および使用量は、反応条件等を勘案して適宜可変するのがよいが、例えば、a、b、c各液の濃度を20重量%とし、この濃度の各液を重量比でa:b:c=5000:42.2:168.5の比率で用いた場合、上記した金属元素重量分率の固溶体粒子が得られる。上記ではこの方法に従って固溶体粒子を作成した。

【0023】また、c液の注加方法の具体例としては、例えばc液の全注加液量を100とした場合、1回目にその1/100、2回目に3/100、3回目に5/100、4回目に7/100、5回目に9/100、6回目に11/100、7回目に13/100、8回目に15/100、9回目に17/100、10回目に19/100というふうに段階的に注加液量を増大させる方法や、高濃度のコバルト塩溶液と低濃度のコバルト塩溶液を用意し、両溶液の混合比率を段階的または連続的に変化させることにより、注加液のコバルト塩濃度を段階的または連続的に高めていく方法が挙げられる。

【0024】更に、上記反応溶液のpHは10~12の範囲で適当に調整すればよいが、反応収率や粒子性状の面から好ましくはpH11とするのがよい。また、反応溶液のpH調整用のアルカリは特に限定されるものではなく、例えば水酸化ナトリウム水溶液のみで行うこともできるが、良好な粒状固溶体を得やすいことから、好ましくはアンモニア水溶液と水酸化ナトリウム水溶液とを併用するのがよい。更にアンモニアと水酸化ナトリウム

の使用比率としては、1:0.05~100(モル比)の範囲がよく、好ましくは1:2~3とするのがよい。

【0025】(本発明被覆活物質粒子BA₀の作製) 上記本発明活物質粒子A₀を約2倍量の硫酸コバルト水溶液(濃度; 10重量%)の中に入れ、攪拌下、水酸化ナトリウム水溶液を反応液pHが10に維持されるように徐々に添加する。これにより活物質粒子A₀の周囲に水酸化コバルトが析出し、粒子の表面が水酸化コバルトで被覆されるので、硫酸コバルト水溶液の添加量を調整して、10重量%(被覆粒子に対する値)の水酸化コバルトを被覆した。この被覆粒子を補集し水洗・乾燥した。以下、この被覆粒子を本発明被覆活物質粒子BA₀とする。

【0026】(比較活物質粒子Xの作製) 上記本発明活物質粒子A₀の作製の場合と同様に、固溶体粒子の全重量を100とすると、亜鉛とコバルトの金属元素重量分率がそれぞれ0.5重量%、2重量%となるように、硫酸ニッケル水溶液(a液)、硫酸亜鉛水溶液(b液)、硫酸コバルト水溶液(c液)を用意した。次にa液、b液及びc液を混合し、攪拌下この混合液に、反応溶液のpHが11に維持されるようにアンモニア水および水酸化ナトリウム水溶液を徐々に添加した。これにより反応溶液中に水酸化ニッケルを主成分とする固溶体粒子が生成・析出するので、これを補集し、水洗・乾燥した。以下、この固溶体粒子を比較活物質粒子Xとする。

【0027】なお、この比較活物質粒子Xと本発明活物質粒子A₀とは、粒子内のコバルト化合物の分布状態が異なり、比較活物質粒子Xではコバルト化合物が粒子内にほぼ均一に分布している。

【0028】(比較被覆活物質粒子BXの作製) 比較活物質粒子Xを用いたこと以外は、本発明活物質粒子BA₀の作製の場合と同様にして、X粒子の表面に水酸化コバルト被覆層を形成した。この粒子を比較被覆活物質粒子BXとする。

【0029】〔各種正極の作製〕

(本発明例正極EA₀の作製) 本発明活物質粒子A₀を90重量部と、水酸化コバルト粉末(平均粒径; 0.20μm)を10重量部と、酸化亜鉛粉末(平均粒径; 0.65μm)を2重量部とを混合し、これに0.2重量%ヒドロキシプロピルセルロース水溶液を50重量部を加えて混練して活物質スラリーを調製した。この活物質スラリーを発泡ニッケル体(多孔度95%、厚み約1.6mm)に充填し乾燥した後、圧延して厚み0.6mmのニッケル正極を作製した。このニッケル正極を、本発明例正極EA₀とする。

【0030】この本発明例正極EA₀は、別途添加した水酸化コバルト含有粉末(水酸化コバルト粉末、酸化亜鉛粉末)が、前記本発明活物質粒子A₀の近傍に存在する状態で正極が構成されている点に特徴を有する。

【0031】なお、上記本発明例正極EA₀では、水酸

化コバルト粉末と酸化亜鉛粉末とからなる水酸化コバルト含有粉末を用いたが、例えば酸化亜鉛以外の他の第三の成分（後記）と水酸化コバルトとの混合末を水酸化コバルト含有粉末として用いることもできるし、水酸化コバルトのみからなる粉末を水酸化コバルト含有粉末として用いることもできる。即ち、本明細書における「水酸化コバルト含有粉末」は、「少なくとも水酸化コバルトを含有した粉末」の意味で使用されている。

【0032】（本発明例正極EBA₀の作製）前記本発明被覆活物質粒子BA₀を用いたこと以外は、上記本発明例正極EA₀の作製と同様にして、本発明例正極EBA₀を作製した。

【0033】この本発明例正極EBA₀と前記正極EA₀とは、組成的には同一であるが、次の点で異なる。即ち、正極EA₀では固溶体粒子A₀と共に10重量%の水酸化コバルトが粉末で添加されているのに対し、正極EBA₀では、10重量%の水酸化コバルトが固溶体粒子A₀の表面に被覆された状態となっている。

【0034】（比較例電極EXの作製）前記比較活物質Xを用いたこと以外は、上記本発明例正極EA₀の作製と同様にして、比較例電極EXを作製した。

【0035】（比較例電極EBXの作製）前記比較活物質粒子BXを用いたこと以外は、上記本発明例正極EA₀の作製と同様にして、比較例電極EBXを作製した。

【0036】なお、上記において、「E」は電極を意味し、例えば「EA₀」は本発明活物質粒子A₀を用いた電極（正極）であることを意味する。また、「B」は、水酸化コバルトが粒子表面に被覆されたものであることを意味し、例えば「BA₀」は本発明活物質粒子A₀を母粒子としこの表面に水酸化コバルト被覆層が形成された活物質であることを意味する。本明細書では全てこの用法に従って活物質、正極の種類が別が表記してある。

【0037】〔電気化学的特性の測定・評価〕上記で作製した各種正極を用いて以下に記載した簡易セルとニッケル水素蓄電池を構成し、これら電池を用いて各種正極活物質の単位活物質重量当たりの放電容量と過放電特性

単位活物質当たり放電容量

=簡易セル放電容量実測値/簡易セルニッケル正極の活物質総量 …数1

【0043】過放電特性は、先ず前記密閉型ニッケル・水素蓄電池に対し、0.1C（120mA）の電流値で16時間充電し、0.2C（240mA）の電流値で電池電圧が1.0Vに達するまで放電するというサイクルを3サイクル繰り返して蓄電池の活性化を行い、この活性化済蓄電池に対し下記条件で充放電を行い、下記数2で過放電特性値を求める方法によった。

【0044】1）1C（1200mA）の電流値で、電池電圧がピークに達し、ピーク電圧値からの電圧降下量（-ΔV値）が10mVに達するまで充電を行う。

2）1時間の休止の後、1Cの電流値で電池電圧が1.

を調べた。

【0038】（簡易セル）上記各種正極とこの正極よりも十分に大きな容量を有する公知の焼結式カドミウム負極とを、不織布からなるセパレータを介して重ね、その両側を内側に加重が掛かる状態にアクリル板で挟み一对の電極体となす。この電極体を電気化学的に過剰量の水酸化カリウム水溶液（濃度：約25重量%）中に浸漬し、理論容量360mAhの開放型簡易セルを構成した。

【0039】（ニッケル水素蓄電池）上記各種正極とこの正極よりも容量の大きい下記の水素吸蔵合金負極とを、不織布からなるセパレータを介して巻回し電極体を作製する。この電極体を電池缶に挿入し、更に7～8.5規定の水酸化カリウム水溶液を注入した後、電池缶開口部を密閉して、理論容量1200mAhの密閉型ニッケル・水素蓄電池を構成した。

【0040】水素吸蔵合金負極の作製方法は次の通りである。Mm、Ni、Co、Al、Mnの各金属元素（市販品）を化学量論比で1:3.4:0.8:0.2:0.6となるように秤量して高周波溶解炉に入れ、混合熔融して水素吸蔵合金鋳塊となし、この合金鋳塊を粗粉碎し更に平均粒径150μm前後まで機械的粉碎した。次いで、この合金粉末にポリエチレンオキサイド（結着剤）と水を適量加えて混練して活物質スラリーとなし、このスラリーをパンチングメタルからなる集電体の両面に塗布・乾燥した後、プレスして厚み約0.4mmの水素吸蔵合金負極を作製した。なお、酸化を防止するため、合金の鋳造、粉碎は不活性ガス雰囲気で行った。

【0041】（電気化学的特性の測定条件）単位活物質重量当たりの放電容量は、簡易セルを0.1C（36mA）の電流値で24時間充電した後、1/3C（120mA）の電流値で電池電圧が1.0Vに達するまで放電してこの時の放電容量を測定し、下記数1に従って算出した。

【0042】

【数1】

0Vに達するまで放電を行う。ここでこの時の放電容量Wi（初回値）を測定しておく。

3）引き続いて0.05C（60mA）の電流値で16時間の強制放電を行う。

4）上記1）～3）の操作を5サイクル繰り返し、5サイクル目の放電容量Wfを測定する。

【0045】

【数2】

過放電特性値=Wf/Wi …数2

【0046】（測定結果）表1に、上記で作製した各種固溶体粒子の組成及び特徴の一覧を示す。また表2に、

これらの固溶体粒子を用いて作製した各種電極の主要成分の組成を示すとともに併せて電気化学的特性に関する試験結果を示す。

【0047】

【表1】

正極活物質 No.	固溶体粒子の組成 (粒子重量に対する金属元素重量%で表示)						水酸化コ バルト被覆層 の有無	備考 固溶体粒子の Co濃度勾配
	Ni	Co	Zn	Cd	Mg	Mn		
A ₀	63.2	2	0.5	—	—	—	なし	有り
BA ₀	63.2	2	0.5	—	—	—	有り*	有り
X	63.2	2	0.5	—	—	—	なし	なし
BX	63.2	2	0.5	—	—	—	有り*	なし

*被覆量：被覆粒子に対し10重量%。

【0048】

【表2】

Ni正極 No.	正極活物質組成 (重量部で表示)			電気化学的特性値	
	固溶体粒子 No.	水酸化コ バルト粉末	酸化亜鉛 粉末	単位活物質当 たり放電容量	過放電係数
EA ₀	A ₀ - 90	10	2	100 (#)	100 (#)
EBA ₀	BA ₀ - 100	—	2	101	99.1
EX	X - 90	10	2	100	94.3
EBX	X - 100	—	2	101	92.5

(# ; 基準)

【0049】表2の正極EA₀とEXの結果において、本発明活物質粒子A₀を用いた正極EA₀は、比較活物質粒子Xを用いた正極EXに比較し、顕著に高い過放電特性値を示した。ここで、正極EA₀と正極EXとは固溶体粒子の作製方法(Co濃度勾配の有無)のみが異なる。したがって、両正極の過放電特性の差は、Co濃度勾配の有無に原因することは明らかであり、このことから、水酸化ニッケルとコバルト化合物を含む固溶体粒子において、粒子中心部に低く粒子表層に高いCo濃度勾配を形成してやると、過放電特性が顕著に高まることが判る。

【0050】ところで、コバルト化合物を濃度勾配をもって固溶体粒子に分散させると過放電特性が向上する理由は、次のように考えられる。正極内に形成される導電ネットワークは、活物質同志の接触によるものである。しかし、活物質粒子の導電性を高めるために、大量のコバルト化合物を配合した場合、粒子の水酸化ニッケル(活物質本体)の密度が低下しエネルギー密度の低下を招く。したがって、導電性改善の目的で配合するコバルト化合物は可能な限り少量の方が好ましく、このためには、コバルト化合物を粒子表面にのみ存在させるのがよい。

【0051】しかし、粒子表面にのみコバルト化合物を存在させた場合、固溶体活物質粒子では、過放電時に粒

子表面のコバルト化合物が粒子内部に拡散し、Co濃度が低下する。これに対し、粒子中心部に低く粒子表面に高いCo濃度勾配を有する固溶体活物質粒子では、粒子表層とその直近内側とのコバルト濃度差が小さいため、コバルトの粒子内部への浸透・拡散が抑制される。また、別途添加され粒子近傍に存在する水酸化コバルト粉末と粒子表面とのコバルト濃度差も小さくできるので、粒子表面近傍に常に高濃度のコバルト化合物を存在させることができる。

【0052】つまり、Co濃度勾配を有する固溶体活物質粒子を用い構成された正極では、水酸化コバルトを介して形成される粒子相互間導電ネットワークが、過放電時においても良好な導電性を維持する。よって、従来の固溶体活物質粒子を用いた正極に比べ、過放電特性が顕著に向上する。

【0053】なお、後記するが、固溶体粒子中に配合された亜鉛化合物等の第三の成分も、過放電時におけるコバルトの拡散を抑制するように作用する。したがって、本発明固溶体活物質粒子では、Co濃度勾配の作用と第三の成分の作用とが合わさって一層良好な過放電特性が得られる。このことからして、この亜鉛化合物をコバルト化合物と同様な方法により濃度勾配を持たせて粒子中に分布させるのも好ましい。

【0054】次に正極EA₀、EXと正極EBA₀、EB

Xの結果を比較検討する。表2において、正極EA₀は、被覆固溶体粒子を用いた正極EBA₀に比べ、過放電特性値がやや低下したものの、単位活物質重量当たりの放電容量がやや向上した。この傾向はEXとEBXとの間でも同様であった。

【0055】ここで、正極EA₀及びEXと、正極EBA₀及びEBXとは被覆層の有無のみが異なり、前者は、水酸化コバルトを粉末で添加したものであり、後者は前者と同一量の水酸化コバルトを固溶体粒子表面に被覆したものである。よって、単に固溶体粒子表面に水酸化コバルトを被覆しただけでは、被覆効果が十分に現れないことが判る。そこで、この結果を踏まえ、以下では水酸化ニッケル、コバルト化合物以外の亜鉛化合物等の第三成分の影響、並びに水酸化コバルト被覆層の処理条件と電気化学的特性の関係を調べ、C₀濃度勾配を有する固溶体粒子の電気化学的特性を更に向上させ得る条件を確立した。以下、検討内容を順次説明する。

【0056】〔第三成分の影響〕第三成分として亜鉛化合物、カドミウム化合物、マグネシウム化合物、マンガン化合物からなる群より選択される化合物を使用し、これらの化合物の1つと水酸化ニッケル及びコバルト化合物とで固溶体粒子（正極活物質粒子A₁～A₄）を作製した。作製方法は第三成分の種類及び配合割合を変化させたこと以外、前記本発明活物質A₀と同様であり、電気化学的特性試験の方法についても前記と同様に行った。

【0057】表3に、第三成分の種類を変えた正極活物質粒子A₁～A₄の組成を示す。また表4に、正極活物質粒子A₁～A₄をそれぞれ用いて前記本発明例正極EA₀と同様にして作製した正極EA₁～EA₄の主要成分の組成、及び電気化学的特性試験の結果を示す。

【0058】

【表3】

正極活物質 No.	固溶体粒子の組成 (粒子重量に対する金属元素重量%で表示)						水酸化コ バルト被覆層 の有無	備考 固溶体粒子の 組成比
	Ni	Co	Zn	Cd	Mg	Mn		
A ₁	61.6	2	2	—	—	—	なし	有り
A ₂	62.0	2	—	2	—	—	なし	有り
A ₃	60.5	2	—	—	2	—	なし	有り
A ₄	61.6	2	—	—	—	2	なし	有り

【0059】

【表4】

Ni正極 No.	正極活物質組成 (重量部で表示)			電気化学的特性値	
	固溶体粒子 No.	水酸化コバ ルト粉末	酸化亜鉛 粉末	単位活物質当 たり放電容量	過放電枚数
EA ₁	A ₁ - 90	10	2	99	103
EA ₂	A ₂ - 90	10	2	98	103
EA ₃	A ₃ - 90	10	2	99	104
EA ₄	A ₄ - 90	10	2	99	102

(前記正極EA₀を100 (重量部) として表示)

【0060】表4において、正極EA₁～EA₄の単位活物質重量当たりの放電容量および過放電特性値に大きな差が認められなかった。他方、EA₁～EA₄の特性値を前記EA₀（表2参照）と比較において、単位活物質重量当たりの放電容量は僅かに低下したものの、過放電特性値は前記EA₀に比較し明確に向上していた。

【0061】ここで、EA₁～EA₄と前記EA₀の違いは、第三成分の配合量のみであるので、上記結果は第三成分量の増加に起因することは明白である。一方、表2の結果と表4の結果から、各固溶体粒子の過放電特性は、固溶体粒子X<固溶体粒子A₀<固溶体粒子A₁～

A₄の順に向上していることが判る。更に本発明者らは、コバルト化合物とともに亜鉛化合物等の第三成分を配合すると、亜鉛化合物等の第三成分が固溶体結晶組織をコバルトの移動しにくい構造とすることを別途見だしている。これらの知見から、次のことが結論できる。

【0062】即ち、亜鉛等の第三成分は、ニッケル・コバルト固溶体結晶組織をコバルトの移動しにくい構造とするプラス作用がある一方、固溶体の水酸化ニッケル密度を低下させ、単位活物質重量当たりの放電容量を低下させるというマイナス作用もある。したがって、A₀（0.5wt%）よりも第三成分の添加量が多いA₁～

A₄ (2wt%)は、第三成分のマイナス作用がある程度現れ、僅かに単位活物質重量当たりの放電容量が低下したものの、第三成分のプラス作用によりA₁～A₄では過放電特性が顕著に向上したものと考えられる。このことから、亜鉛等の第三成分の作用を都合良く発揮させるためには、第三成分の配合量を適正にする必要があるが、亜鉛化合物等の第三成分量を2% (金属元素重量%表示)とした場合には、単位活物質重量当たりの放電容量を殆ど低下させることなく、C₀濃度勾配の作用との共働作用により過放電時におけるコバルト化合物の固溶体内移動を有効に抑制することができる。

【0063】〔水酸化コバルト被覆層の処理条件〕被覆固溶体粒子(BA₀)に以下の条件でアルカリ熱処理を実施して、一層電気化学的特性を高め得る条件を検討した。

【0064】(アルカリ熱処理条件)前記被覆活物質粒子BA₀に25重量%の水酸化ナトリウム水溶液を含浸させた後、各温度の加熱空气中で3時間熱処理し、アルカリ熱処理済の被覆活物質粒子H-1、H-2、H-3、H-4、H-5、H-6を作製した。また、アルカリの種類と影響を調べるため、上記水酸化ナトリウム水溶液の代わりに25重量%の水酸化カリウム水溶液を用い、加熱温度を80℃とし、その他の条件を上記と同様にしてアルカリ熱処理済被覆活物質粒子H-7を作製した。

【0065】次いで、上記各粒子を用い正極EBA₀の場合と同様にして正極を作製するとともに、前記と同様な方法で電気化学的特性を調べた。その結果を、アルカリ熱処理条件とともに表5に示す。

【0066】

〔表5〕

	アルカリ熱処理条件		電気化学的特性値	
	アルカリの種類	加熱温度℃	単位活物質当たり放電容量	過放電指数
H-1	NaOH	30	101.0	99.1
H-2	NaOH	40	104.0	101.0
H-3	NaOH	60	107.1	103.0
H-4	NaOH	80	106.1	103.0
H-5	NaOH	100	104.0	101.0
H-6	NaOH	120	98.0	98.1
H-7	KOH	80	107.1	104.0

(被覆固溶体粒子BA₀を使用。前記正極EBA₀を100(基準)として表示)

【0067】表5において、アルカリ熱処理を実施した被覆活物質粒子H-2、H-3、H-4、H-5は、非アルカリ熱処理の被覆活物質粒子BA₀ (表2参照)に比較し、単位活物質重量当たりの放電容量、過放電特性値の何れ

もが向上していた。しかし、H-1 (熱処理温度30℃)は、BA₀と同様な特性値を示し、H-6 (熱処理温度120℃)では、単位活物質重量当たりの放電容量が低下していた。このことから、アルカリ熱処理温度は40℃～100℃とするのが好ましく、被覆活物質粒子にこの条件でアルカリ熱処理を行った場合、電気化学的特性が顕著に高まる。

【0068】他方、水酸化カリウム水溶液を用いてアルカリ熱処理を行ったH-7は、H-2～H-5よりも更に優れた電気化学的特性を示した。このことから、アルカリ熱処理におけるアルカリ金属としては、好ましくは水酸化カリウムを使用するのがよい。

【0069】なお、アルカリ熱処理によって電気化学的特性が向上するのは、被覆層のコバルト化合物が導電性に優れる2価以上の高次コバルト化合物に変化し、また被覆層が電解液と馴染み易い性状に変化するためと考えられる。

【発明の効果】以上に説明したように、本発明にかかる固溶体活物質粒子では、コバルト化合物が濃度勾配をもって活物質粒子中に分布し、かつ粒子表面に高濃度に存在するように構成されている。したがって、コバルト化合物が粒子全体に均一に分散した従来の固溶体活物質粒子に比べ、少ない量のコバルト化合物の配合でもって効率良く粒子導電性を向上させることができ、しかも粒子表面とその内側直近さらにその内側直近 (以下同様) とのコバルト濃度差が少ないので、粒子表面のコバルト化合物が充放電に伴って粒子内部に拡散しにくい。

【0070】更に、この固溶体活物質粒子には、亜鉛化合物、カドミウム化合物、マグネシウム化合物、マンガ化合物からなる群より選択される1種以上の化合物 (第三の成分) が配合してあるので、この化合物がコバルト化合物の拡散を抑制するように作用して上記C₀濃度勾配の効果を増強する。

【0071】更にまた、このような特性を有する固溶体活物質粒子を主成分とし、これに別途水酸化コバルト粉末を配合してなる本発明正極活物質では、上記の説明と同様理由から、粉末添加のコバルト化合物が充放電ともなって活物質粒子内部に拡散して減少することがない。したがって、粒子表面近傍に常に高濃度に存在する水酸化コバルトが、粒子相互間の導電性を好適に維持する。

【0072】一方、本発明にかかる被覆活物質粒子では、水酸化コバルトを粉末で添加することに代え、水酸化コバルトを粒子表面に被覆してある。このような被覆活物質粒子では、水酸化コバルトが常に粒子表面に密着した状態で存在しているので、水酸化コバルトを粉末で添加する場合に比べ、水酸化コバルトの導電性向上効果が有利に発揮される。

【0073】更に、本発明では、このような被覆活物質粒子をアルカリ熱処理して、被覆層を好適な性状に改質

し、一層の電気化学的特性の向上を図ってある。即ち、被覆活物質粒子に対しアルカリ熱処理を施した場合、被覆層を構成するコバルト化合物がより導電性に優れた2価以上のコバルト化合物に変化するとともに、被覆層がポーラスなものとなり電解液との接触性が良くなる。したがって、このような被覆活物質粒子で正極を構成した場合、正極内に好適な導電ネットワークが形成され、かつ電解液との接触性もよいので、上記C○濃度勾配の効果や第三の成分の効果も加わって、いわゆるペースト式における欠点である集電効率が改善され、電極活物質の

利用率が大幅に向上すると共に、単位活物質重量当たりの電気容量（エネルギー密度）が高まる。そしてこの効果は、特に過放電時において顕著に発揮される。

【0074】また、本発明製造方法によれば、比較的簡易な方法で確実かつ安定して上記のような優れた固溶体活物質粒子および被覆活物質粒子を製造できる。よって、単位活物質重量当たりの電気容量が高く、かつ過放電特性に優れたアルカリ蓄電池用正極活物質を安価に供給できるという効果が得られる。

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(54) POSITIVE ACTIVE MATERIAL FOR ALKALINE STORAGE BATTERY AND MANUFACTURE THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To enhance conductivity between active material particles with the small amount of cobalt compound by forming concentration gradient so that the concentration of the cobalt compound is high on the surface of a solid solution particle and gradually decreased toward the central part of the particle.

SOLUTION: Nickel sulfate aqueous solution ((a) solution), zinc sulfate aqueous solution ((b) solution), and cobalt sulfate solution ((c) solution) are prepared so that the element weight fraction of zinc and that of cobalt are 0.5wt.% and 2wt.% respectively when the whole weight of solid solution particle is 100. The (a) solution and the (b) solution are mixed and stirred, and the (c) solution is added to the mixture so that the pouring amount per time is increased continuously or by stages. At the same time, ammonia water and sodium hydroxide aqueous solution are gradually added so that pH of (a), (b), and (c) solutions is kept in the specified value. Solid solution particle comprising compounds of nickel, zinc, and cobalt is obtained, and the cobalt compound is dispersed in the particle so as to have such concentration gradient that the concentration of the cobalt compound is low on the inside of the particle and high on the surface of the particle.

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CLAIMS

[Claim(s)]

[Claim 1] It is the positive active material for alkaline batteries characterized by being the positive active material for alkaline batteries which uses as an indispensable component the solid-solution particle which contains nickel hydroxide and a cobalt compound at least, and said solid-solution particle having the cobalt concentration gradient which decreases toward a particle core highly on a particle surface.

[Claim 2] Said solid-solution particle is positive active material for alkaline batteries according to claim 1 with which the cobalt hydroxide enveloping layer which has the cobalt concentration of a particle surface and the cobalt concentration more than an EQC is further characterized by what is formed in a particle front face.

[Claim 3] The cobalt hydroxide in said cobalt hydroxide enveloping layer is positive active material for alkaline batteries according to claim 2 characterized by considering as the cobalt compound exceeding divalent by heat-treating the solid-solution particle in which the enveloping layer was formed under coexistence of alkali and oxygen.

[Claim 4] Said positive active material for alkaline batteries is positive active material for alkaline batteries according to claim 1 characterized by including said solid-solution particle and the cobalt hydroxide content powder which has the cobalt concentration of said solid-solution particle surface, and the cobalt concentration more than an EQC.

[Claim 5] Said solid-solution particle is claim 1 characterized by what one or more sorts of compounds further chosen from the group which consists of a zinc compound, cadmium compounds, a magnesium compound, and a manganese compound are contained for thru/or the positive active material for alkaline batteries according to claim 4.

[Claim 6] In the manufacture approach of the solid-solution active material particle for alkaline batteries which comes to contain nickel hydroxide and a cobalt compound at least the manufacture approach of said solid-solution active material particle for alkaline batteries By pouring a cobalt salt solution to the bottom nickel salt solution of stirring, so that a cobalt salt addition may increase continuously or gradually, pouring an alkali solution in concurrency with this, and maintaining the reaction solution pH to a predetermined value The manufacture approach of the solid-solution active material particle for alkaline batteries characterized by having the solid-solution particle making process which produces the nickel cobalt solid-solution particle which has a low cobalt concentration gradient high on a particle surface in a particle core.

[Claim 7] The manufacture approach of the solid-solution active material particle for alkaline batteries according to claim 6 characterized by making ammonia exist in a reaction solution in said solid-solution particle making process.

[Claim 8] The manufacture approach of claim 6 which carries out stirring distribution at the cobalt

salt solution which dissolved cobalt salt for said nickel cobalt solid-solution particle at least, and is characterized by what a cobalt compound is deposited and it has further for the enveloping layer formation process which forms a cobalt hydroxide enveloping layer in the front face of said nickel cobalt solid-solution particle by pouring an alkali solution into this stirring dispersion liquid, and adjusting dispersion liquid pH to a predetermined value through/or the solid-solution active material particle for alkaline batteries according to claim 7.

[Claim 9] Furthermore, the manufacture approach of the solid-solution active material particle for alkaline batteries according to claim 8 is characterized by what it has the alkali heat treatment process heat-treated under oxygen existence for after carrying out impregnation of the alkali-metal solution to the coat solid-solution particle produced with said enveloping layer formation process.

[Claim 10] The manufacture approach of the solid-solution active material particle for alkaline batteries according to claim 9 that said alkali-metal solution is characterized by being a potassium hydroxide solution.

[Claim 11] The manufacture approach of claim 9 to which temperature of said heat treatment is characterized by being 40-100 degrees C through/or the solid-solution active material particle for alkaline batteries according to claim 10.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a solid-solution particle and amelioration of the made nickel hydroxide active material with nickel hydroxide and a cobalt compound in detail about the positive active material for alkaline batteries.

[0002]

[Description of the Prior Art] There are the so-called sintering type which fills up with an active material the sintering type substrate which sintered nickel powder, and the so-called paste type which fills up the nickel porous body of high porosity, such as a nickel fiber sintering porous body and a foaming nickel porous body, with a paste-like active material in the process of the nickel positive electrode for alkaline batteries. However, a sintering type has complicated restoration of an active material, and since a limitation is in high porosity of a substrate, it has the fault of being hard to attain high energy consistency of an electrode. For this reason, in recent years, the paste-type nickel positive electrode using a high porosity nickel object is becoming in use in order to respond to the request of the formation of a high energy consistency of a cell, and low-pricing.

[0003] However, although the high density restoration to a porous body is possible for a paste type, since its pole diameter of the porous body which functions as a charge collector is large, it becomes inadequate electric contacting it a porous body and an active material, and it has the fault that current collection effectiveness is bad. For this reason, there is a problem [capacity / of the active material with which high density was filled up / generation-of-electrical-energy] that there is enough no cash-drawer profit.

[0004] Then, it aims at improving the fault of such a paste type conventionally. ** The technique (JP,62-222566,A) which forms the enveloping layer of cobalt hydroxide in the front face of the solid-solution active material powder containing nickel hydroxide, cadmium hydroxide, or cobalt hydroxide, ** Consider as the technique (JP,3-62457,A) which forms the solid solution of nickel hydroxide and cobalt hydroxide in the surface section of nickel hydroxide, and the technique which improved the technique of a publication further to said JP,62-222566,A further. ** The technique (JP,5-151962,A) of giving the hydrophilic organic substance film on the enveloping layer

containing the cobalt compound formed in the nickel hydroxide front face etc. is proposed. Since active material particle mutual conductivity improves when these techniques are applied, the engine performance of a nickel positive electrode can be raised.

[0005]

[Problem(s) to be Solved by the Invention] However, with the above-mentioned technique, the following troubles are not solvable. That is, although this cobalt hydroxide raises the conductivity between active material particles when cobalt hydroxide is arranged on a nickel hydroxide particle front face, the cobalt hydroxide on the front face of a particle is diffused inside nickel hydroxide at the time of over discharge, and the phenomenon in which the amount of cobalt hydroxide on the front face of a particle decreases produces it. For this reason, the conductivity of an active material particle falls, that utilization factor falls, and there is a problem of it becoming impossible to take out sufficient cell capacity especially at the time of over discharge. In order to cause relative reduction of the amount of nickel hydroxide (amount of the body of an active material), it becomes impossible however, to fully raise an energy density by the approach of counting upon said diffusion and arranging a lot of cobalt hydroxide on a particle front face or the whole active material beforehand.

[0006] Moreover, since the technique of the aforementioned ** is a technique in which it prevents physically that a cobalt kind dissipates into the electrolytic solution by giving the hydrophilic organic substance film on an enveloping layer, it cannot control the phenomenon diffused inside a mother particle also with this technique.

[0007] This invention aims at offering the manufacture approach of the positive active material for alkaline batteries which is made in order to solve the trouble in said conventional technique, is effectively raised as a small quantity of a cobalt compound is also about the conductivity between active material particles, and the cobalt compound near the mother particle front face does not diffuse inside a nickel hydroxide mother particle at the time of over discharge, and such positive active material for alkaline batteries.

[0008]

[Means for Solving the Problem] In order to attain the above-mentioned object, this invention has the following description. Invention according to claim 1 is positive active material for alkaline batteries which uses as an indispensable component the solid-solution particle which contains nickel hydroxide and a cobalt compound at least, and said solid-solution particle is characterized by having the cobalt concentration gradient which decreases toward a particle core highly on a particle surface.

[0009] Invention according to claim 2 is characterized by forming in the front face of said solid-solution particle the cobalt hydroxide enveloping layer which has the cobalt concentration of a particle surface, and the cobalt concentration more than an EQC in the positive active material for alkaline batteries according to claim 1.

[0010] Invention according to claim 3 is positive active material for alkaline batteries according to claim 2 characterized by having considered as the cobalt compound with which the cobalt hydroxide in said cobalt hydroxide enveloping layer exceeds divalent by heat-treating the solid-solution particle in which the enveloping layer was formed under coexistence of alkali and oxygen.

[0011] Invention according to claim 4 is characterized by the positive active material for alkaline batteries according to claim 1 containing said solid-solution particle and the cobalt hydroxide content powder which has the cobalt concentration of said solid-solution particle surface, and the cobalt concentration more than an EQC.

[0012] Invention according to claim 5 is characterized by containing one or more sorts of compounds chosen from the group which said solid-solution particle becomes from a zinc compound, cadmium compounds, a magnesium compound, and a manganese compound further in

claim 1 thru/or the positive active material for alkaline batteries according to claim 4.

[0013] To the bottom nickel salt solution of stirring, invention according to claim 6 pours a cobalt salt solution so that it may increase continuously [a cobalt salt addition] or gradually. By pouring an alkali solution in concurrency with this, and maintaining the reaction solution pH to a predetermined value [0014] characterized by being the manufacture approach of the solid-solution active material particle for alkaline batteries equipped with the solid-solution particle making process which produces the nickel cobalt solid-solution particle which has a low cobalt concentration gradient high on a particle surface in a particle core Invention according to claim 7 is characterized by making ammonia exist in a reaction solution in the solid-solution particle making process of the manufacture approach of the solid-solution active material particle for alkaline batteries according to claim 6.

[0015] Invention according to claim 8 is set to the manufacture approach of claim 6 thru/or the solid-solution active material particle for alkaline batteries according to claim 7. Furthermore, stirring distribution of said nickel cobalt solid-solution particle is carried out at the cobalt salt solution which dissolved cobalt salt at least. By pouring an alkali solution into these stirring dispersion liquid, and adjusting dispersion liquid pH to a predetermined value, a cobalt compound is deposited and it is characterized by having the enveloping layer formation process which forms a cobalt hydroxide enveloping layer in the front face of said nickel cobalt solid-solution particle.

[0016] In the manufacture approach of the solid-solution active material particle for alkaline batteries according to claim 8, after invention according to claim 9 carries out impregnation of the alkali-metal solution to the coat solid-solution particle produced with said enveloping layer formation process further, it is characterized by having the alkali heat treatment process heat-treated under oxygen existence.

[0017] Invention according to claim 10 is characterized by said alkali-metal solution being a potassium hydroxide solution in the manufacture approach of the solid-solution active material particle for alkaline batteries according to claim 9.

[0018] Invention according to claim 11 is characterized by the temperature of said heat treatment being 40-100 degrees C in the manufacture approach of claim 9 thru/or the solid-solution active material particle for alkaline batteries according to claim 10.

[0019]

[Embodiment of the Invention] The gestalt of operation of this invention is clarified by explaining the production approach of the nickel solid-solution active material particle concerning this invention, and the manufacture approach of the positive electrode using this solid-solution active material particle hereafter, and explaining the electrochemical property of various solid-solution active material particles by the cell which incorporated this positive electrode after that.

[0020] [Production of various solid-solution active material particles]

(Production of this invention active material particle A0) First, when setting total weight of a solid-solution particle to 100, the nickel-sulfate water solution (a liquid), the zinc-sulfate water solution (b liquid), and the cobalt sulfate water solution (c liquid) were prepared so that the metallic element weight fraction of zinc and cobalt might become 0.5 % of the weight and 2 % of the weight, respectively. Next, while adding said c liquid, controlling the amount of pouring to increase gradually [the amount of pouring per unit time amount], or continuously, carrying out stirring mixing of said a liquid and b liquid, and continuing stirring mixing to this ab liquid, aqueous ammonia and a sodium-hydroxide water solution were gradually added so that pH of an abc reaction solution might be maintained by the predetermined value in concurrency with this. Since the active material particle which uses nickel hydroxide as a principal component into an abc reaction solution by this generated and deposited, this was extracted, it rinsed and dried and the nickel cobalt solid-solution particle was obtained. It is this invention active material particle A0

about this following and nickel cobalt solid-solution particle. It carries out.

[0021] When each solution is made to react by the approach of increasing gradually or continuously the amount of pouring of c liquid to ab liquid as mentioned above, the solid-solution particle which consists of three components of a nickel compound, a zinc compound, and a cobalt compound is obtained, and this solid-solution particle becomes what the cobalt compound distributed in the particle with the concentration gradient (henceforth Co concentration gradient) low and high on a particle front face inside the particle.

[0022] In addition, although the concentration and the amount of each liquid of the above a, b, and c used are good to take a reaction condition etc. into consideration and to carry out adjustable suitably, when concentration of a, b, and c each liquid is made into 20 % of the weight and each liquid of this concentration is used by the ratio of a:b:c=5000:42.2:168.5 by the weight ratio for example, the solid-solution particle of the above-mentioned metallic element weight fraction is obtained. In the above, the solid-solution particle was created according to this approach.

[0023] Moreover, when all the pouring volume of c liquid is set to 100 as an example of the pouring approach of c liquid, for example, To the 1st time at its 1 / the 100 or 2nd time 3/100, To the 3rd time, 5 / method of increasing [7 / the 100 or 5th time / 11 / the 100 or 7th time / 13 / the 100 or 8th time / 15 / the 100 or 9th time / 17 / the 100 or 10th time / **** of 19/100] pouring volume gradually to 9 / the 100 or 6th time the 100 or 4th time, The approach of raising the cobalt salt concentration of pouring liquid gradually or continuously is mentioned by preparing a high-concentration cobalt salt solution and a low-concentration cobalt salt solution, and changing the mixed ratio of both solutions gradually or continuously.

[0024] Furthermore, although what is necessary is just to adjust pH of the above-mentioned reaction solution suitably in 10-12, it is good to be preferably referred to as pH11 from the field of the shape of reaction yield or corpuscular character. Moreover, although especially the alkali for pH adjustment of a reaction solution is not limited and only a sodium-hydroxide water solution can also perform it, it is good to use together an aqueous ammonia solution and a sodium-hydroxide water solution preferably from it being easy to obtain the good granular solid solution. Furthermore, as a rate of an use rate of ammonia and a sodium hydroxide, the range of 1:0.05-100 (mole ratio) is good, and it is good to be preferably referred to as 1:2-3.

[0025] (Production of this invention coat active material particle BA 0) The above-mentioned this invention active material particle A0 It puts in into the cobalt sulfate water solution (concentration; 10 % of the weight) of the amount of about 2 times, and under stirring, a sodium-hydroxide water solution is gradually added, as reaction mixture pH maintained in 10. Thereby, it is the active material particle A0. Since cobalt hydroxide deposited around and the front face of a particle was covered with cobalt hydroxide, the addition of a cobalt sulfate water solution was adjusted and 10% of the weight (value over a coated particle) of cobalt hydroxide was covered. The collection of this coated particle was carried out, and it rinsed and dried. It is this invention coat active material particle BA 0 about the following and this coated particle. It carries out.

[0026] (Production of the comparison active material particle X) Above-mentioned this invention active material particle A₀ Like the case of production, when setting total weight of a solid-solution particle to 100, the nickel-sulfate water solution (a liquid), the zinc-sulfate water solution (b liquid), and the cobalt sulfate water solution (c liquid) were prepared so that the metallic element weight fraction of zinc and cobalt might become 0.5 % of the weight and 2 % of the weight, respectively. Next, a liquid, b liquid, and c liquid were mixed, and under stirring, aqueous ammonia and a sodium-hydroxide water solution were gradually added so that pH of a reaction solution might be maintained by this mixed liquor 11. Since the solid-solution particle which uses nickel hydroxide as a principal component into a reaction solution by this generated and deposited, the collection of this was carried out, and it rinsed and dried. Hereafter, let this solid-solution particle be the

comparison active material particle X.

[0027] In addition, this comparison active material particle X and this invention active material particle A0 The distribution conditions of the cobalt compound in a particle differ, and the cobalt compound is mostly distributed in a particle by the comparison active material particle X at homogeneity.

[0028] (Production of the comparison coat active material particle BX) Except having used the comparison active material particle X, it is this invention active material particle BA 0. The cobalt hydroxide enveloping layer was formed in the front face of X particle like the case of production. Let this particle be the comparison coat active material particle BX.

[0029] [Production of various positive electrodes]

(Production of the example positive electrode EA0 of this invention) this invention active material particle A0 Two weight sections were mixed [cobalt hydroxide powder (mean particle diameter; 0.20 micrometers)] with 90 weight sections for zinc-oxide powder (mean particle diameter; 0.65 micrometers) with 10 weight sections, to this, the hydroxypropylcellulose water solution was added 0.2% of the weight, 50 weight sections were kneaded, and the active material slurry was prepared. After filling up the foaming nickel object (porosity of 95%, thickness of about 1.6mm) with this active material slurry and drying, it rolled out and the nickel positive electrode with a thickness of 0.6mm was produced. About this nickel positive electrode, it is the example positive electrode EA0 of this invention. It carries out.

[0030] This example positive electrode EA0 of this invention The cobalt hydroxide content powder (cobalt hydroxide powder, zinc-oxide powder) added separately is said this invention active material particle A0. It has the description at the point that the positive electrode consists of conditions of existing in near.

[0031] in addition, the above-mentioned example positive electrode EA0 of this invention **** -- although the cobalt hydroxide content powder which consists of cobalt hydroxide powder and zinc oxide powder was used, the mixed end of other third component other than a zinc oxide (postscript) and cobalt hydroxide can also be used as cobalt hydroxide content powder, for example, and the powder which consists only of cobalt hydroxide can also be used as cobalt hydroxide content powder. Namely, the "cobalt hydroxide content powder" in this description is used in the sense of "the powder which contained cobalt hydroxide at least."

[0032] (Production of the example positive electrode EBA 0 of this invention) Said this invention coat active material particle BA 0 It is the example positive electrode EBA 0 of this invention like production of the above-mentioned example positive electrode EA0 of this invention except having used. It produced.

[0033] This example positive electrode EBA 0 of this invention Said positive electrode EA0 Although it is the same in presentation, it differs the following point. Namely, positive electrode EA0 It is the solid-solution particle A0 then. It is a positive electrode EBA 0 to 10% of the weight of cobalt hydroxide being added with powder. 10% of the weight of cobalt hydroxide is the solid-solution particle A0. It is in the condition of having been covered by the front face.

[0034] (Production of the example electrode EX of a comparison) Except having used said comparison active material X, it is the above-mentioned example positive electrode EA0 of this invention. The example electrode EX of a comparison was produced like production.

[0035] (Production of the example electrode EBX of a comparison) Except having used said comparison active material particle BX, it is the above-mentioned example positive electrode EA0 of this invention. The example electrode EBX of a comparison was produced like production.

[0036] in addition, the above -- setting -- "E" -- an electrode -- meaning -- for example, "EA0" -- this invention active material particle A0 It means that it is the used electrode (positive electrode). moreover, the thing for which, as for "B", cobalt hydroxide is covered by the particle front face --

meaning -- for example, "BA0" -- this invention active material particle A0 It means that it is the active material with which it considered as the mother particle and the cobalt hydroxide enveloping layer was formed in this front face. On these descriptions, the exception of the class of an active material and positive electrode is altogether written according to this direction for use.

[0037] [Measurement and assessment] of an electrochemical property The simple cell and nickel hydrogen battery which were indicated below using the various positive electrodes produced above were constituted, and the discharge capacity and the over discharge property per unit active material weight of various positive active material were investigated using these cells.

[0038] (Simple cell) The various above-mentioned positive electrodes and the well-known sintering type cadmium negative electrode which has a capacity bigger enough than this positive electrode are piled up through the separator which consists of a non-woven fabric, those both sides are inserted into the condition that a load is applied inside, with an acrylic board, and it makes with the electrode object of a couple. This electrode object was electrochemically immersed into the potassium-hydroxide water solution (concentration; about 25 % of the weight) of an excessive amount, and the open sand mold simple cell of geometric capacity 360mAh was constituted.

[0039] (Nickel hydrogen battery) A winding electrode object is produced through the separator which consists the various above-mentioned positive electrodes and the following hydrogen storing metal alloy negative electrode with a larger capacity than this positive electrode of a non-woven fabric. After inserting this electrode object in the cell can and pouring in the potassium-hydroxide water solution of further seven to 8.5 convention, cell can opening was sealed and the closed mold nickel and the hydrogen battery of geometric capacity 1200mAh were constituted.

[0040] The production approach of a hydrogen storing metal alloy negative electrode is as follows. Weighing capacity of each metallic element (commercial item) of Mm, nickel, Co, aluminum, and Mn was carried out so that it might be set to 1:3.4:0.8:0.2:0.6 by the stoichiometrical ratio, it was put into the RF fusion furnace, mixed fusion was carried out, coarse grinding of a hydrogen storing metal alloy ingot, and nothing and this alloy ingot was carried out, and mechanical grinding was further carried out before and behind the mean particle diameter of 150 micrometers. Subsequently, after applying and drying polyethylene oxide (binder) and water in the end of this alloy powder to optimum dose, in addition both sides of a charge collector which knead and consist an active material slurry, and nothing and this slurry of a punching metal, it pressed and the hydrogen storing metal alloy negative electrode with a thickness of about 0.4mm was produced. In addition, in order to prevent oxidation, casting of an alloy and grinding were performed under the inert gas ambient atmosphere.

[0041] (Measuring condition of an electrochemical property) After the discharge capacity per unit active material weight charged the simple cell with the current value of 0.1C (36mA) for 24 hours, it discharged until cell voltage amounted to 1.0V in the current value of 1/3C (120mA), it measured the discharge capacity at this time, and computed it according to the one following.

[0042]

[Equation 1]

単位活物質当たり放電容量

=簡易セル放電容量実測値/簡易セルニッケル正極の活物質総量 …数1

[0043] The over discharge property was based on the approach of charging with the current value of 0.1C (120mA) to said closed mold nickel and hydrogen battery for 16 hours first, activating 3 cycle repeat ***** for the cycle of discharging until cell voltage amounts to 1.0V in the current value of 0.2C (240mA), performing charge and discharge on the following conditions to this activated battery, and calculating over discharge weighted solidity by the two following.

[0044] 1) Charge until cell voltage reaches a peak and the amount of voltage drops from a peak

voltage value (-delta V value) amounts to 10mV in the current value of 1C (1200mA).

2) Discharge after the pause of 1 hour until cell voltage amounts to 1.0V in the current value of 1C. The discharge capacity Wi (first time value) at this time is measured here.

3) Perform compulsive discharge of 16 hours with the current value of 0.05C (60mA) succeeding.

4) It is the discharge capacity Wf of 5 cycle repeat and 5 cycle eye about actuation of the above 1-3. It measures.

[0045]

[Equation 2]

過放電特性値 = Wf / Wi …数2

[0046] (Measurement result) The presentation of the various solid-solution particles produced above and the list of the descriptions are shown in a table 1. Moreover, while the presentation of the major component of the various electrodes which used and produced these solid-solution particles is shown in a table 2, the test result about an electrochemical property is shown collectively.

[0047]

[A table 1]

正極活物質 No.	固溶体粒子の組成 (粒子重量に対する金属元素重量%で表示)						水酸化コバルト被覆層 の有無	備考 固溶体粒子の Co濃度分配
	Ni	Co	Zn	Cd	Mg	Mn		
A ₀	63.2	2	0.5	—	—	—	なし	有り
BA ₀	63.2	2	0.5	—	—	—	有り*	有り
X	63.2	2	0.5	—	—	—	なし	なし
BX	63.2	2	0.5	—	—	—	有り*	なし

*被覆量：被覆粒子に対し10重量%。

[0048]

[A table 2]

Ni正極 No.	正極活物質組成 (重量部で表示)			電気化学的特性値	
	固溶体粒子 No.	水酸化コバルト粉末	酸化亜鉛粉末	単位活物質当 たり放電容量	過放電指数
EA ₀	A ₀ - 90	10	2	100 (#)	100 (#)
EBA ₀	BA ₀ -100	—	2	101	99.1
EX	X - 90	10	2	100	94.3
EBX	X - 100	—	2	101	92.5

(# ; 基準)

[0049] Positive electrode EA0 of a table 2 It sets to the result of EX and is this invention active material particle A0. Used positive electrode EA0 Notably high over discharge weighted solidity was shown as compared with the positive electrode EX using the comparison active material particle X. Here, it is a positive electrode EA0. As for a positive electrode EX, only the production approaches (existence of Co concentration gradient) of a solid-solution particle differ. Therefore, when the difference of result [from the existence of Co concentration gradient] of the over

discharge property of both positive electrodes is clear and low Co concentration gradient high on a particle surface is formed in a particle core in the solid-solution particle containing nickel hydroxide and a cobalt compound from this, it turns out that an over discharge property increases notably.

[0050] By the way, the reason whose over discharge property will improve if a solid-solution particle is made to distribute a cobalt compound with a concentration gradient is considered as follows. The electric conduction network formed in a positive electrode is based on contact of an active material comrade. However, in order to raise the conductivity of an active material particle, when the cobalt compound of a large quantity is blended, the consistency of the nickel hydroxide (body of an active material) of a particle falls, and lowering of an energy density is caused. Therefore, as for the cobalt compound blended for the object of a conductive improvement, a little is more desirable as much as possible, and, for that, it is good to make a cobalt compound exist only in a particle front face.

[0051] However, when a cobalt compound is made to exist only in a particle front face, by the solid-solution active material particle, the cobalt compound on the front face of a particle is spread inside a particle at the time of over discharge, and Co concentration falls. On the other hand, by the solid-solution active material particle which has low Co concentration gradient high on a particle front face in a particle core, since the cobalt concentration difference a particle surface and by the side of the direct Konnai is small, osmosis and diffusion inside [of cobalt] a particle are controlled. Moreover, since the cobalt concentration difference of the cobalt hydroxide powder and particle front face which are added separately and exist near the particle can also be made small, a high-concentration cobalt compound can be made to always exist near the particle front face.

[0052] That is, in the positive electrode constituted using the solid-solution active material particle which has Co concentration gradient, the between [particles] electric conduction network formed through cobalt hydroxide maintains good conductivity at the time of over discharge. Therefore, compared with the positive electrode using the conventional solid-solution active material particle, an over discharge property improves notably.

[0053] In addition, although a postscript is carried out, the third component, such as a zinc compound blended into the solid-solution particle, also acts so that diffusion of the cobalt at the time of over discharge may be controlled. Therefore, by this invention solid-solution active material particle, an operation of Co concentration gradient and an operation of the third component are put together, and a much more good over discharge property is acquired. Considering this, it is also desirable to give a concentration gradient by the same approach as a cobalt compound, and to distribute this zinc compound in a particle.

[0054] Next, comparison examination of the result of a positive electrode EA0, and the EX and positive electrodes EBA and EBX 0 is carried out. It sets to a table 2 and is a positive electrode EA0. Positive electrode EBA 0 using a coat solid-solution particle Although it compared and over discharge weighted solidity fell a little, the discharge capacity per unit active material weight improved a little. This inclination was the same also between EX and EBX.

[0055] Here, it is a positive electrode EA0. And EX and a positive electrode EBA 0 And only the existence of an enveloping layer differs, the former adds cobalt hydroxide with powder, and, as for EBX, the latter covers the cobalt hydroxide of the same amount as the former on a solid-solution particle front face. Therefore, it turns out that covering effect does not fully show up only by covering cobalt hydroxide on a solid-solution particle front face. Then, based on this result, the relation between the processing conditions of a cobalt hydroxide enveloping layer and an electrochemical property was investigated in the effect of the third component, such as zinc compounds other than nickel hydroxide and a cobalt compound, and a list, and, below, the conditions which may raise further the electrochemical property of a solid-solution particle of having Co concentration gradient were established. Hereafter, sequential explanation of the content

of examination is given.

[0056] [Effect of the third component] The compound chosen from the group which consists of a zinc compound, cadmium compounds, a magnesium compound, and a manganese compound as the third component was used, and the solid-solution particle (the positive-active-material particle A1 - A4) was produced with one, the nickel hydroxide, and the cobalt compound of these compounds. The production approach is said this invention active material A0 except having changed the third class and blending ratio of coal of a component. It is the same and carried out about the approach of an electrochemical characteristic test as well as the above.

[0057] The positive-active-material particle A1 - A4 which changed the class of third component into a table 3 A presentation is shown. Moreover, to a table 4, they are the positive-active-material particle A1 - A4. Positive-electrode EA1 -EA4 which used, respectively and was produced like said example positive electrode EA0 of this invention The presentation of a major component and the result of an electrochemical characteristic test are shown.

[0058]

[A table 3]

正極活性物質 No.	固溶体粒子の組成 (粒子重量に対する金属元素重量%で表示)						水酸化コバルト被覆層 の有無	備考 固溶体粒子の Co濃度を配
	Ni	Co	Zn	Cd	Mg	Mn		
A ₁	61.6	2	2	—	—	—	なし	有り
A ₂	62.0	2	—	2	—	—	なし	有り
A ₃	60.5	2	—	—	2	—	なし	有り
A ₄	61.6	2	—	—	—	2	なし	有り

[0059]

[A table 4]

Ni正極 No.	正極活性物質組成 (重量部で表示)			電気化学的特性値	
	固溶体粒子 No.	水酸化コバルト粉末	酸化亜鉛粉末	単位活性物質当 たり放電容量	過放電指数
EA ₁	A ₁ - 90	10	2	99	103
EA ₂	A ₂ - 90	10	2	98	103
EA ₃	A ₃ - 90	10	2	99	104
EA ₄	A ₄ - 90	10	2	99	102

(前記正極EA₀を100 (基準) として表示)

[0060] It sets to a table 4 and is positive-electrode EA1 -EA4. A big difference was not accepted in the discharge capacity and over discharge weighted solidity per unit active material weight. On the other hand, EA1 -EA4 Although the discharge capacity per unit active material weight fell weighted solidity slightly in said EA0 (table 2 reference) and comparison, over discharge weighted solidity is said EA0. It compared and was improving clearly.

[0061] Here, it is EA1 -EA4. Said EA0 Since a difference is only the loadings of the third component, as for the above-mentioned result, it is clear to originate in the increment in the amount of third components. On the other hand, the over discharge property of the result of a table 2 and the

result of a table 4 to each solid-solution particle is the solid-solution particle X < solid-solution particle A0 < solid-solution particle A1 - A4. It turns out that it is improving in order. Furthermore, this invention persons have found out separately that the third components, such as a zinc compound, consider as the structure where cobalt cannot move the solid-solution crystalline structure easily, if the third components, such as a zinc compound, are blended with a cobalt compound. The following thing can be concluded from these knowledge.

[0062] That is, while the third components, such as zinc, have the plus operation made into the structure where cobalt cannot move the nickel cobalt solid-solution crystalline structure easily, they also have a minus operation of reducing the nickel hydroxide consistency of the solid solution and reducing the discharge capacity per unit active material weight. Therefore, it is thought that the over discharge property of A4 [A1 with more additions of the third component than A0 (0.5wt%) -] (2wt%) improved notably by A1 - A4 according to a plus operation of the third component although the minus operation of the third component appeared to some extent and the discharge capacity per unit active material weight fell slightly. Although it is necessary to make the loadings of the third component proper in order to demonstrate an operation of the third components, such as zinc, with sufficient convenience from this, the solid-solution internal transmigration of the cobalt compound at the time of over discharge can be effectively controlled according to a having-two-incomes operation with an operation of Co concentration gradient, without reducing most discharge capacity per unit active material weight, when the amounts of third components, such as a zinc compound, are made into 2% (metallic element weight % display).

[0063] [Processing conditions of a cobalt hydroxide enveloping layer] Alkali heat treatment was carried out on condition that the following to the coat solid-solution particle (BA0), and the conditions which can raise an electrochemical property further were examined.

[0064] (Alkali heat treatment conditions) Said coat active material particle BA 0 The coat active material particle [finishing / heat-treat in the heating air of each temperature for 3 hours, and / alkali heat treatment / after carrying out impregnation of 25% of the weight of the sodium-hydroxide water solution] H-1, H-2, H-3, H-4, H-5, and H-6 It produced. Moreover, in order to investigate the class and effect of alkali, 25% of the weight of the hydroxylation KARIUMUMU water solution was used instead of the above-mentioned sodium-hydroxide water solution, whenever [stoving temperature] was made into 80 degrees C, and the heat-treated [alkali] coat active material particle H-7 was produced for other conditions like the above.

[0065] Subsequently, each above-mentioned particle is used and it is a positive electrode EBA 0. While producing the positive electrode like the case, the electrochemical property was investigated by the same approach as the above. The result is shown in a table 5 with alkali heat treatment conditions.

[0066]

[A table 5]

	アルカリ熱処理条件		電気化学的特性値	
	アルカリの種類	加熱温度℃	単位活物質当たり放電容量	過放電指数
H-1	NaOH	30	101.0	99.1
H-2	NaOH	40	104.0	101.0
H-3	NaOH	60	107.1	103.0
H-4	NaOH	80	106.1	103.0
H-5	NaOH	100	104.0	101.0
H-6	NaOH	120	98.0	98.1
H-7	KOH	80	107.1	104.0

(被覆固体粒子BA₀を使用。前記電極EA₀を100(基準)として表示)

[0067] the coat active material particle H-2 which carried out alkali heat treatment in a table 5, H-3, H-4, and H-5 -- the coat active material particle BA 0 (table 2 reference) of non-alkali heat treatment -- comparing -- both the discharge capacity per unit active material weight, and over discharge weighted solidity -- although -- it was improving. However, H-1 (heat treatment temperature of 30 degrees C) is BA0. The same weighted solidity was shown and the discharge capacity per unit active material weight was falling in H-6 (heat treatment temperature of 120 degrees C). When it is desirable to consider as 40 degrees C - 100 degrees C as for alkali heat treatment temperature and alkali heat treatment is performed to a coat active material particle on this condition from this, an electrochemical property increases notably.

[0068] On the other hand, H-7 which performed alkali heat treatment using the potassium-hydroxide water solution showed the electrochemical property which was further superior to H-2 to H-5. It is good to use a potassium hydroxide preferably as an alkali metal in alkali heat treatment from this.

[0069] In addition, it thinks to change to the high order cobalt compound more than divalent [the cobalt compound of an enveloping layer excels / divalent / in conductivity], and for an enveloping layer to change to the electrolytic solution and the description it is easy to get used to, and it is **** that an electrochemical property improves by alkali heat treatment.

[Effect of the Invention] As explained above, it consists of solid-solution active material particles concerning this invention so that a cobalt compound may be distributed in an active material particle with a concentration gradient and it may exist in a particle surface at high concentration. therefore, compared with the conventional solid-solution active material particle which the cobalt compound distributed to homogeneity at the whole particle, particle conductivity can be efficiently raised as combination of a small quantity of a cobalt compound is also, and since particle surfaces and the inside direct nearness of those have few cobalt concentration differences with the inside latest (the following -- the same), in connection with charge and discharge, it is hard to diffuse the cobalt compound on the front face of a particle inside a particle moreover.

[0070] Furthermore, since one or more sorts of compounds (the third component) chosen as this solid-solution active material particle from the group which consists of a zinc compound, cadmium compounds, a magnesium compound, and a manganese compound are blended, it acts so that this compound may control diffusion of a cobalt compound, and the effectiveness of the above-mentioned Co concentration gradient is reinforced.

[0071] Furthermore, like the above-mentioned explanation, in connection with charge and discharge, the solid-solution active material particle which has such a property again is used as a principal component, and they do not decrease in number [the cobalt compounds of powder addition are spread and] inside an active material particle from a reason in this invention positive active material which comes to blend cobalt hydroxide powder with this separately. Therefore, the cobalt hydroxide which always exists in high concentration near the particle front face maintains the conductivity between particles suitably.

[0072] On the other hand, cobalt hydroxide is replaced with adding with powder, and cobalt hydroxide is covered with the coat active material particle concerning this invention on the particle front face. By such coat active material particle, since it exists after cobalt hydroxide has always stuck to the particle front face, compared with the case where cobalt hydroxide is added with powder, the conductive improvement effectiveness of cobalt hydroxide is demonstrated advantageously.

[0073] Furthermore, in this invention, alkali heat treatment of such a coat active material particle is carried out, an enveloping layer is reformed to suitable description, and there is drawing about improvement in much more electrochemical property. That is, when alkali heat treatment is performed to a coat active material particle, while the cobalt compound which constitutes an enveloping layer changes to the cobalt compound more than divalent [which was more excellent in conductivity], an enveloping layer will become porous and contact nature with the electrolytic solution will become good. therefore , when a positive electrode be constitute from such a coat active material particle , an electric conduction network suitable in a positive electrode be form , and since contact nature with the electrolytic solution be also good , while the effectiveness of the above-mentioned Co concentration gradient and the effectiveness of the third component be also add , the current collection effectiveness be a fault in the so-called paste type be improve and the utilization factor of an electrode active material improve substantially , the electric capacity per unit active material weight (an energy density) increase . And especially this effectiveness is notably demonstrated at the time of over discharge.

[0074] moreover, certain by the comparatively simple approach according to this invention manufacture approach -- and it is stabilized and the above outstanding solid-solution active material particles and coat active material particles can be manufactured. Therefore, the effectiveness that the electric capacity per unit active material weight is high, and can supply cheaply the positive active material for alkaline batteries excellent in the over discharge property is acquired.

TECHNICAL FIELD

[Field of the Invention] This invention relates to a solid-solution particle and amelioration of the made nickel hydroxide active material with nickel hydroxide and a cobalt compound in detail about the positive active material for alkaline batteries.

[Description of the Prior Art] There are the so-called sintering type which fills up with an active material the sintering type substrate which sintered nickel powder, and the so-called paste type which fills up the nickel porous body of high porosity, such as a nickel fiber sintering porous body and a foaming nickel porous body, with a paste-like active material in the process of the nickel positive electrode for alkaline batteries. However, a sintering type has complicated restoration of an active material, and since a limitation is in high porosity of a substrate, it has the fault of being hard to attain high energy consistency of an electrode. For this reason, in recent years, the paste-type nickel positive electrode using a high porosity nickel object is becoming in use in order to respond to the request of the formation of a high energy consistency of a cell, and low-pricing.

[0003] However, although the high density restoration to a porous body is possible for a paste type, since its pole diameter of the porous body which functions as a charge collector is large, it becomes inadequate electric contacting it a porous body and an active material, and it has the fault that current collection effectiveness is bad. For this reason, there is a problem [capacity / of the active material with which high density was filled up / generation-of-electrical-energy] that there is enough no cash-drawer profit.

[0004] Then, it aims at improving the fault of such a paste type conventionally. ** The technique (JP,62-222566,A) which forms the enveloping layer of cobalt hydroxide in the front face of the solid-solution active material powder containing nickel hydroxide, cadmium hydroxide, or cobalt hydroxide, ** Consider as the technique (JP,3-62457,A) which forms the solid solution of nickel hydroxide and cobalt hydroxide in the surface section of nickel hydroxide, and the technique which improved the technique of a publication further to said JP,62-222566,A further. ** The technique (JP,5-151962,A) of giving the hydrophilic organic substance film on the enveloping layer containing the cobalt compound formed in the nickel hydroxide front face etc. is proposed. Since active material particle mutual conductivity improves when these techniques are applied, the engine performance of a nickel positive electrode can be raised.

EFFECT OF THE INVENTION

[Effect of the Invention] As explained above, it consists of solid-solution active material particles concerning this invention so that a cobalt compound may be distributed in an active material particle with a concentration gradient and it may exist in a particle surface at high concentration. therefore, compared with the conventional solid-solution active material particle which the cobalt compound distributed to homogeneity at the whole particle, particle conductivity can be efficiently raised as combination of a small quantity of a cobalt compound is also, and since particle surfaces and the inside direct nearness of those have few cobalt concentration differences with the inside latest (the following -- the same), in connection with charge and discharge, it is hard to diffuse the cobalt compound on the front face of a particle inside a particle moreover.

[0070] Furthermore, since one or more sorts of compounds (the third component) chosen as this solid-solution active material particle from the group which consists of a zinc compound, cadmium compounds, a magnesium compound, and a manganese compound are blended, it acts so that this compound may control diffusion of a cobalt compound, and the effectiveness of the above-mentioned Co concentration gradient is reinforced.

[0071] Furthermore, like the above-mentioned explanation, in connection with charge and discharge, the solid-solution active material particle which has such a property again is used as a principal component, and they do not decrease in number [the cobalt compounds of powder addition are spread and] inside an active material particle from a reason in this invention positive active material which comes to blend cobalt hydroxide powder with this separately. Therefore, the cobalt hydroxide which always exists in high concentration near the particle front face maintains the conductivity between particles suitably.

[0072] On the other hand, cobalt hydroxide is replaced with adding with powder, and cobalt hydroxide is covered with the coat active material particle concerning this invention on the particle front face. By such coat active material particle, since it exists after cobalt hydroxide has always stuck to the particle front face, compared with the case where cobalt hydroxide is added with powder, the conductive improvement effectiveness of cobalt hydroxide is demonstrated advantageously.

[0073] Furthermore, in this invention, alkali heat treatment of such a coat active material particle is carried out, an enveloping layer is reformed to suitable description, and there is drawing about

improvement in much more electrochemical property. That is, when alkali heat treatment is performed to a coat active material particle, while the cobalt compound which constitutes an enveloping layer changes to the cobalt compound more than divalent [which was more excellent in conductivity], an enveloping layer will become porous and contact nature with the electrolytic solution will become good. therefore , when a positive electrode be constitute from such a coat active material particle , an electric conduction network suitable in a positive electrode be form , and since contact nature with the electrolytic solution be also good , while the effectiveness of the above-mentioned Co concentration gradient and the effectiveness of the third component be also add , the current collection effectiveness be a fault in the so-called paste type be improve and the utilization factor of an electrode active material improve substantially , the electric capacity per unit active material weight (an energy density) increase . And especially this effectiveness is notably demonstrated at the time of over discharge.

[0074] moreover, certain by the comparatively simple approach according to this invention manufacture approach -- and it is stabilized and the above outstanding solid-solution active material particles and coat active material particles can be manufactured. Therefore, the effectiveness that the electric capacity per unit active material weight is high, and can supply cheaply the positive active material for alkaline batteries excellent in the over discharge property is acquired.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, with the above-mentioned technique, the following troubles are not solvable. That is, although this cobalt hydroxide raises the conductivity between active material particles when cobalt hydroxide is arranged on a nickel hydroxide particle front face, the cobalt hydroxide on the front face of a particle is diffused inside nickel hydroxide at the time of over discharge, and the phenomenon in which the amount of cobalt hydroxide on the front face of a particle decreases produces it. For this reason, the conductivity of an active material particle falls, that utilization factor falls, and there is a problem of it becoming impossible to take out sufficient cell capacity especially at the time of over discharge. In order to cause relative reduction of the amount of nickel hydroxide (amount of the body of an active material), it becomes impossible however, to fully raise an energy density by the approach of counting upon said diffusion and arranging a lot of cobalt hydroxide on a particle front face or the whole active material beforehand.

[0006] Moreover, since the technique of the aforementioned ** is a technique in which it prevents physically that a cobalt kind dissipates into the electrolytic solution by giving the hydrophilic organic substance film on an enveloping layer, it cannot control the phenomenon diffused inside a mother particle also with this technique.

[0007] This invention aims at offering the manufacture approach of the positive active material for alkaline batteries which is made in order to solve the trouble in said conventional technique, is effectively raised as a small quantity of a cobalt compound is also about the conductivity between active material particles, and the cobalt compound near the mother particle front face does not diffuse inside a nickel hydroxide mother particle at the time of over discharge, and such positive active material for alkaline batteries.

MEANS

[Means for Solving the Problem] In order to attain the above-mentioned object, this invention has the following description. Invention according to claim 1 is positive active material for alkaline batteries which uses as an indispensable component the solid-solution particle which contains nickel

hydroxide and a cobalt compound at least, and said solid-solution particle is characterized by having the cobalt concentration gradient which decreases toward a particle core highly on a particle surface.

[0009] Invention according to claim 2 is characterized by forming in the front face of said solid-solution particle the cobalt hydroxide enveloping layer which has the cobalt concentration of a particle surface, and the cobalt concentration more than an EQC in the positive active material for alkaline batteries according to claim 1.

[0010] Invention according to claim 3 is positive active material for alkaline batteries according to claim 2 characterized by having considered as the cobalt compound with which the cobalt hydroxide in said cobalt hydroxide enveloping layer exceeds divalent by heat-treating the solid-solution particle in which the enveloping layer was formed under coexistence of alkali and oxygen.

[0011] Invention according to claim 4 is characterized by the positive active material for alkaline batteries according to claim 1 containing said solid-solution particle and the cobalt hydroxide content powder which has the cobalt concentration of said solid-solution particle surface, and the cobalt concentration more than an EQC.

[0012] Invention according to claim 5 is characterized by containing one or more sorts of compounds chosen from the group which said solid-solution particle becomes from a zinc compound, cadmium compounds, a magnesium compound, and a manganese compound further in claim 1 thru/or the positive active material for alkaline batteries according to claim 4.

[0013] To the bottom nickel salt solution of stirring, invention according to claim 6 pours a cobalt salt solution so that it may increase continuously [a cobalt salt addition] or gradually. By pouring an alkali solution in concurrency with this, and maintaining the reaction solution pH to a predetermined value [0014] characterized by being the manufacture approach of the solid-solution active material particle for alkaline batteries equipped with the solid-solution particle making process which produces the nickel cobalt solid-solution particle which has a low cobalt concentration gradient high on a particle surface in a particle core Invention according to claim 7 is characterized by making ammonia exist in a reaction solution in the solid-solution particle making process of the manufacture approach of the solid-solution active material particle for alkaline batteries according to claim 6.

[0015] Invention according to claim 8 is set to the manufacture approach of claim 6 thru/or the solid-solution active material particle for alkaline batteries according to claim 7. Furthermore, stirring distribution of said nickel cobalt solid-solution particle is carried out at the cobalt salt solution which dissolved cobalt salt at least. By pouring an alkali solution into these stirring dispersion liquid, and adjusting dispersion liquid pH to a predetermined value, a cobalt compound is deposited and it is characterized by having the enveloping layer formation process which forms a cobalt hydroxide enveloping layer in the front face of said nickel cobalt solid-solution particle.

[0016] In the manufacture approach of the solid-solution active material particle for alkaline batteries according to claim 8, after invention according to claim 9 carries out impregnation of the alkali-metal solution to the coat solid-solution particle produced with said enveloping layer formation process further, it is characterized by having the alkali heat treatment process heat-treated under oxygen existence.

[0017] Invention according to claim 10 is characterized by said alkali-metal solution being a potassium hydroxide solution in the manufacture approach of the solid-solution active material particle for alkaline batteries according to claim 9.

[0018] Invention according to claim 11 is characterized by the temperature of said heat treatment being 40-100 degrees C in the manufacture approach of claim 9 thru/or the solid-solution active material particle for alkaline batteries according to claim 10.

[0019]

[Embodiment of the Invention] The gestalt of operation of this invention is clarified by explaining the production approach of the nickel solid-solution active material particle concerning this invention, and the manufacture approach of the positive electrode using this solid-solution active material particle hereafter, and explaining the electrochemical property of various solid-solution active material particles by the cell which incorporated this positive electrode after that.

[0020] [Production of various solid-solution active material particles]

(Production of this invention active material particle A0) First, when setting total weight of a solid-solution particle to 100, the nickel-sulfate water solution (a liquid), the zinc-sulfate water solution (b liquid), and the cobalt sulfate water solution (c liquid) were prepared so that the metallic element weight fraction of zinc and cobalt might become 0.5 % of the weight and 2 % of the weight, respectively. Next, while adding said c liquid, controlling the amount of pouring to increase gradually [the amount of pouring per unit time amount], or continuously, carrying out stirring mixing of said a liquid and b liquid, and continuing stirring mixing to this ab liquid, aqueous ammonia and a sodium-hydroxide water solution were gradually added so that pH of an abc reaction solution might be maintained by the predetermined value in concurrency with this. Since the active material particle which uses nickel hydroxide as a principal component into an abc reaction solution by this generated and deposited, this was extracted, it rinsed and dried and the nickel cobalt solid-solution particle was obtained. It is this invention active material particle A0 about this following and nickel cobalt solid-solution particle. It carries out.

[0021] When each solution is made to react by the approach of increasing gradually or continuously the amount of pouring of c liquid to ab liquid as mentioned above, the solid-solution particle which consists of three components of a nickel compound, a zinc compound, and a cobalt compound is obtained, and this solid-solution particle becomes what the cobalt compound distributed in the particle with the concentration gradient (henceforth Co concentration gradient) low and high on a particle front face inside the particle.

[0022] In addition, although the concentration and the amount of each liquid of the above a, b, and c used are good to take a reaction condition etc. into consideration and to carry out adjustable suitably, when concentration of a, b, and c each liquid is made into 20 % of the weight and each liquid of this concentration is used by the ratio of a:b:c=5000:42.2:168.5 by the weight ratio for example, the solid-solution particle of the above-mentioned metallic element weight fraction is obtained. In the above, the solid-solution particle was created according to this approach.

[0023] Moreover, when all the pouring volume of c liquid is set to 100 as an example of the pouring approach of c liquid, for example, To the 1st time at its 1 / the 100 or 2nd time 3/100, To the 3rd time, 5 / method of increasing [7 / the 100 or 5th time / 11 / the 100 or 7th time / 13 / the 100 or 8th time / 15 / the 100 or 9th time / 17 / the 100 or 10th time / **** of 19/100] pouring volume gradually to 9 / the 100 or 6th time the 100 or 4th time, The approach of raising the cobalt salt concentration of pouring liquid gradually or continuously is mentioned by preparing a high-concentration cobalt salt solution and a low-concentration cobalt salt solution, and changing the mixed ratio of both solutions gradually or continuously.

[0024] Furthermore, although what is necessary is just to adjust pH of the above-mentioned reaction solution suitably in 10-12, it is good to be preferably referred to as pH11 from the field of the shape of reaction yield or corpuscular character. Moreover, although especially the alkali for pH adjustment of a reaction solution is not limited and only a sodium-hydroxide water solution can also perform it, it is good to use together an aqueous ammonia solution and a sodium-hydroxide water solution preferably from it being easy to obtain the good granular solid solution. Furthermore, as a rate of an use rate of ammonia and a sodium hydroxide, the range of 1:0.05-100 (mole ratio) is good, and it is good to be preferably referred to as 1:2-3.

[0025] (Production of this invention coat active material particle BA 0) The above-mentioned this

invention active material particle A0 It puts in into the cobalt sulfate water solution (concentration; 10 % of the weight) of the amount of about 2 times, and under stirring, a sodium-hydroxide water solution is gradually added, as reaction mixture pH maintained in 10. Thereby, it is the active material particle A0. Since cobalt hydroxide deposited around and the front face of a particle was covered with cobalt hydroxide, the addition of a cobalt sulfate water solution was adjusted and 10% of the weight (value over a coated particle) of cobalt hydroxide was covered. The collection of this coated particle was carried out, and it rinsed and dried. It is this invention coat active material particle BA 0 about the following and this coated particle. It carries out.

[0026] (Production of the comparison active material particle X) The above-mentioned this invention active material particle A0 Like the case of production, when setting total weight of a solid-solution particle to 100, the nickel-sulfate water solution (a liquid), the zinc-sulfate water solution (b liquid), and the cobalt sulfate water solution (c liquid) were prepared so that the metallic element weight fraction of zinc and cobalt might become 0.5 % of the weight and 2 % of the weight, respectively. Next, a liquid, b liquid, and c liquid were mixed, and under stirring, aqueous ammonia and a sodium-hydroxide water solution were gradually added so that pH of a reaction solution might be maintained by this mixed liquor 11. Since the solid-solution particle which uses nickel hydroxide as a principal component into a reaction solution by this generated and deposited, the collection of this was carried out, and it rinsed and dried. Hereafter, let this solid-solution particle be the comparison active material particle X.

[0027] In addition, this comparison active material particle X and this invention active material particle A0 The distribution conditions of the cobalt compound in a particle differ, and the cobalt compound is mostly distributed in a particle by the comparison active material particle X at homogeneity.

[0028] (Production of the comparison coat active material particle BX) Except having used the comparison active material particle X, it is this invention active material particle BA 0. The cobalt hydroxide enveloping layer was formed in the front face of X particle like the case of production. Let this particle be the comparison coat active material particle BX.

[0029] [Production of various positive electrodes]

(Production of the example positive electrode EA0 of this invention) this invention active material particle A0 Two weight sections were mixed [cobalt hydroxide powder (mean particle diameter; 0.20 micrometers)] with 90 weight sections for zinc-oxide powder (mean particle diameter; 0.65 micrometers) with 10 weight sections, to this, the hydroxypropylcellulose water solution was added 0.2% of the weight, 50 weight sections were kneaded, and the active material slurry was prepared. After filling up the foaming nickel object (porosity of 95%, thickness of about 1.6mm) with this active material slurry and drying, it rolled out and the nickel positive electrode with a thickness of 0.6mm was produced. About this nickel positive electrode, it is the example positive electrode EA0 of this invention. It carries out.

[0030] This example positive electrode EA0 of this invention The cobalt hydroxide content powder (cobalt hydroxide powder, zinc-oxide powder) added separately is said this invention active material particle A0. It has the description at the point that the positive electrode consists of conditions of existing in near.

[0031] in addition, the above-mentioned example positive electrode EA0 of this invention **** -- although the cobalt hydroxide content powder which consists of cobalt hydroxide powder and zinc oxide powder was used, the mixed end of other third component other than a zinc oxide (postscript) and cobalt hydroxide can also be used as cobalt hydroxide content powder, for example, and the powder which consists only of cobalt hydroxide can also be used as cobalt hydroxide content powder. Namely, the "cobalt hydroxide content powder" in this description is used in the sense of "the powder which contained cobalt hydroxide at least."

[0032] (Production of the example positive electrode EBA 0 of this invention) Said this invention coat active material particle BA 0 It is the example positive electrode EBA 0 of this invention like production of the above-mentioned example positive electrode EA0 of this invention except having used. It produced.

[0033] This example positive electrode EBA 0 of this invention Said positive electrode EA0 Although it is the same in presentation, it differs the following point. Namely, positive electrode EA0 It is the solid-solution particle A0 then. It is a positive electrode EBA 0 to 10% of the weight of cobalt hydroxide being added with powder. 10% of the weight of cobalt hydroxide is the solid-solution particle A0. It is in the condition of having been covered by the front face.

[0034] (Production of the example electrode EX of a comparison) Except having used said comparison active material X, it is the above-mentioned example positive electrode EA0 of this invention. The example electrode EX of a comparison was produced like production.

[0035] (Production of the example electrode EBX of a comparison) Except having used said comparison active material particle BX, it is the above-mentioned example positive electrode EA0 of this invention. The example electrode EBX of a comparison was produced like production.

[0036] in addition, the above -- setting -- "E" -- an electrode -- meaning -- for example, "EA0" -- this invention active material particle A0 It means that it is the used electrode (positive electrode). moreover, the thing for which, as for "B", cobalt hydroxide is covered by the particle front face -- meaning -- for example, "BA0" -- this invention active material particle A0 It means that it is the active material with which it considered as the mother particle and the cobalt hydroxide enveloping layer was formed in this front face. On these descriptions, the exception of the class of an active material and positive electrode is altogether written according to this direction for use.

[0037] [Measurement and assessment] of an electrochemical property The simple cell and nickel hydrogen battery which were indicated below using the various positive electrodes produced above were constituted, and the discharge capacity and the over discharge property per unit active material weight of various positive active material were investigated using these cells.

[0038] (Simple cel) The various above-mentioned positive electrodes and the well-known sintering type cadmium negative electrode which has a capacity bigger enough than this positive electrode are piled up through the separator which consists of a non-woven fabric, those both sides are inserted into the condition that a load is applied inside, with an acrylic board, and it makes with the electrode object of a couple. This electrode object was electrochemically immersed into the potassium-hydroxide water solution (concentration; about 25 % of the weight) of an excessive amount, and the open sand mold simple cell of geometric capacity 360mAh was constituted.

[0039] (Nickel hydrogen battery) A winding electrode object is produced through the separator which consists the various above-mentioned positive electrodes and the following hydrogen storing metal alloy negative electrode with a larger capacity than this positive electrode of a non-woven fabric. After inserting this electrode object in the cell can and pouring in the potassium-hydroxide water solution of further seven to 8.5 convention, cell can opening was sealed and the closed mold nickel and the hydrogen battery of geometric capacity 1200mAh were constituted.

[0040] The production approach of a hydrogen storing metal alloy negative electrode is as follows. Weighing capacity of each metallic element (commercial item) of Mm, nickel, Co, aluminum, and Mn was carried out so that it might be set to 1:3.4:0.8:0.2:0.6 by the stoichiometrical ratio, it was put into the RF fusion furnace, mixed fusion was carried out, coarse grinding of a hydrogen storing metal alloy ingot, and nothing and this alloy ingot was carried out, and mechanical grinding was further carried out before and behind the mean particle diameter of 150 micrometers. Subsequently, after applying and drying polyethylene oxide (binder) and water in the end of this alloy powder to optimum dose, in addition both sides of a charge collector which knead and consist an active material slurry, and nothing and this slurry of a punching metal, it pressed and the hydrogen storing

metal alloy negative electrode with a thickness of about 0.4mm was produced. In addition, in order to prevent oxidation, casting of an alloy and grinding were performed under the inert gas ambient atmosphere.

[0041] (Measuring condition of an electrochemical property) After the discharge capacity per unit active material weight charged the simple cell with the current value of 0.1C (36mA) for 24 hours, it discharged until cell voltage amounted to 1.0V in the current value of 1/3C (120mA), it measured the discharge capacity at this time, and computed it according to the one following.

[0042]

[Equation 1]

単位活物質当たり放電容量

=簡易セル放電容量実測値/簡易セルニッケル正極の活物質総量 …数1

[0043] The over discharge property was based on the approach of charging with the current value of 0.1C (120mA) to said closed mold nickel and hydrogen battery for 16 hours first, activating 3 cycle repeat ***** for the cycle of discharging until cell voltage amounts to 1.0V in the current value of 0.2C (240mA), performing charge and discharge on the following conditions to this activated battery, and calculating over discharge weighted solidity by the two following.

[0044] 1) Charge until cell voltage reaches a peak and the amount of voltage drops from a peak voltage value (-delta V value) amounts to 10mV in the current value of 1C (1200mA).

2) Discharge after the pause of 1 hour until cell voltage amounts to 1.0V in the current value of 1C. The discharge capacity Wi (first time value) at this time is measured here.

3) Perform compulsive discharge of 16 hours with the current value of 0.05C (60mA) succeeding.

4) It is the discharge capacity Wf of 5 cycle repeat and 5 cycle eye about actuation of the above 1-3. It measures.

[0045]

[Equation 2]

過放電特性値=Wf /Wi …数2

[0046] (Measurement result) The presentation of the various solid-solution particles produced above and the list of the descriptions are shown in a table 1. Moreover, while the presentation of the major component of the various electrodes which used and produced these solid-solution particles is shown in a table 2, the test result about an electrochemical property is shown collectively.

[0047]

[A table 1]

正極活物質 No.	固溶体粒子の組成 (粒子重量に対する金属元素重量%で表示)						水酸化コバルト被覆層 の有無	備考 固溶体粒子の Co濃度%配
	Ni	Co	Zn	Cd	Mg	Mn		
A ₀	63.2	2	0.5	—	—	—	なし	有り
BA ₀	63.2	2	0.5	—	—	—	有り*	有り
X	63.2	2	0.5	—	—	—	なし	なし
BX	63.2	2	0.5	—	—	—	有り*	なし

*被覆量:被覆粒子に対し10重量%.

[0048]

[A table 2]

Ni正極 No.	正極活性物質組成 (重量部で表示)			電気化学的特性値	
	固溶体粒子 No.	水酸化コバ ルト粉末	酸化亜鉛 粉末	単位活性物質当 たり放電容量	過放電指数
EA ₀	A ₀ - 90	10	2	100 (#)	100 (#)
EBA ₀	BA ₀ -100	—	2	101	99.1
EX	X - 90	10	2	100	94.3
EBX	X - 100	—	2	101	92.5

(# ; 基準)

[0049] Positive electrode EA₀ of a table 2 It sets to the result of EX and is this invention active material particle A₀. Used positive electrode EA₀ Notably high over discharge weighted solidity was shown as compared with the positive electrode EX using the comparison active material particle X. Here, it is a positive electrode EA₀. As for a positive electrode EX, only the production approaches (existence of Co concentration gradient) of a solid-solution particle differ. Therefore, when the difference of result [from the existence of Co concentration gradient] of the over discharge property of both positive electrodes is clear and low Co concentration gradient high on a particle surface is formed in a particle core in the solid-solution particle containing nickel hydroxide and a cobalt compound from this, it turns out that an over discharge property increases notably.

[0050] By the way, the reason whose over discharge property will improve if a solid-solution particle is made to distribute a cobalt compound with a concentration gradient is considered as follows. The electric conduction network formed in a positive electrode is based on contact of an active material comrade. However, in order to raise the conductivity of an active material particle, when the cobalt compound of a large quantity is blended, the consistency of the nickel hydroxide (body of an active material) of a particle falls, and lowering of an energy density is caused. Therefore, as for the cobalt compound blended for the object of a conductive improvement, a little is more desirable as much as possible, and, for that, it is good to make a cobalt compound exist only in a particle front face.

[0051] However, when a cobalt compound is made to exist only in a particle front face, by the solid-solution active material particle, the cobalt compound on the front face of a particle is spread inside a particle at the time of over discharge, and Co concentration falls. On the other hand, by the solid-solution active material particle which has low Co concentration gradient high on a particle front face in a particle core, since the cobalt concentration difference a particle surface and by the side of the direct Konnai is small, osmosis and diffusion inside [of cobalt] a particle are controlled. Moreover, since the cobalt concentration difference of the cobalt hydroxide powder and particle front face which are added separately and exist near the particle can also be made small, a high-concentration cobalt compound can be made to always exist near the particle front face.

[0052] That is, in the positive electrode constituted using the solid-solution active material particle which has Co concentration gradient, the between [particles] electric conduction network formed through cobalt hydroxide maintains good conductivity at the time of over discharge. Therefore, compared with the positive electrode using the conventional solid-solution active material particle, an over discharge property improves notably.

[0053] In addition; although a postscript is carried out, the third component, such as a zinc compound blended into the solid-solution particle, also acts so that diffusion of the cobalt at the time of over discharge may be controlled. Therefore, by this invention solid-solution active material particle, an operation of Co concentration gradient and an operation of the third component are put

together, and a much more good over discharge property is acquired. Considering this, it is also desirable to give a concentration gradient by the same approach as a cobalt compound, and to distribute this zinc compound in a particle.

[0054] Next, comparison examination of the result of a positive electrode EA0, and the EX and positive electrodes EBA and EBX 0 is carried out. It sets to a table 2 and is a positive electrode EA0. Positive electrode EBA 0 using a coat solid-solution particle Although it compared and over discharge weighted solidity fell a little, the discharge capacity per unit active material weight improved a little. This inclination was the same also between EX and EBX.

[0055] Here, it is a positive electrode EA0. And EX and a positive electrode EBA 0 And only the existence of an enveloping layer differs, the former adds cobalt hydroxide with powder, and, as for EBX, the latter covers the cobalt hydroxide of the same amount as the former on a solid-solution particle front face. Therefore, it turns out that covering effect does not fully show up only by covering cobalt hydroxide on a solid-solution particle front face. Then, based on this result, the relation between the processing conditions of a cobalt hydroxide enveloping layer and an electrochemical property was investigated in the effect of the third component, such as zinc compounds other than nickel hydroxide and a cobalt compound, and a list, and, below, the conditions which may raise further the electrochemical property of a solid-solution particle of having Co concentration gradient were established. Hereafter, sequential explanation of the content of examination is given.

[0056] [Effect of the third component] The compound chosen from the group which consists of a zinc compound, cadmium compounds, a magnesium compound, and a manganese compound as the third component was used, and the solid-solution particle (the positive-active-material particle A1 - A4) was produced with one, the nickel hydroxide, and the cobalt compound of these compounds. The production approach is said this invention active material A0 except having changed the third class and blending ratio of coal of a component. It is the same and carried out about the approach of an electrochemical characteristic test as well as the above.

[0057] The positive-active-material particle A1 - A4 which changed the class of third component into a table 3 A presentation is shown. Moreover, to a table 4, they are the positive-active-material particle A1 - A4. Positive-electrode EA1 -EA4 which used, respectively and was produced like said example positive electrode EA0 of this invention The presentation of a major component and the result of an electrochemical characteristic test are shown.

[0058]

[A table 3]

正極活性物質 No.	固溶体粒子の組成 (粒子重量に対する金属元素重量%で表示)						水酸化コバルト被覆層 の有無	備考 固溶体粒子の Co濃度と配
	Ni	Co	Zn	Cd	Mg	Mn		
A ₁	61.6	2	2	—	—	—	なし	有り
A ₂	62.0	2	—	2	—	—	なし	有り
A ₃	60.5	2	—	—	2	—	なし	有り
A ₄	61.6	2	—	—	—	2	なし	有り

[0059]

[A table 4]

Ni正極 No.	正極活性物質組成 (重量部で表示)			電気化学的特性値	
	固溶体粒子 No.	水酸化コバルト粉末	酸化亜鉛粉末	単位活性物質当 たり放電容量	過放電指数
EA ₁	A ₁ - 90	10	2	99	103
EA ₂	A ₂ - 90	10	2	98	103
EA ₃	A ₃ - 90	10	2	99	104
EA ₄	A ₄ - 90	10	2	99	102

(前記電極EA₀を100 (基準) として表示)

[0060] It sets to a table 4 and is positive-electrode EA1 -EA4. A big difference was not accepted in the discharge capacity and over discharge weighted solidity per unit active material weight. On the other hand, EA1 -EA4 Although the discharge capacity per unit active material weight fell weighted solidity slightly in said EA0 (table 2 reference) and comparison, over discharge weighted solidity is said EA0. It compared and was improving clearly.

[0061] Here, it is EA1 -EA4. Said EA0 Since a difference is only the loadings of the third component, as for the above-mentioned result, it is clear to originate in the increment in the amount of third components. On the other hand, the over discharge property of the result of a table 2 and the result of a table 4 to each solid-solution particle is the solid-solution particle X< solid-solution particle A0 < solid-solution particle A1 - A4. It turns out that it is improving in order. Furthermore, this invention persons have found out separately that the third components, such as a zinc compound, consider as the structure where cobalt cannot move the solid-solution crystalline structure easily, if the third components, such as a zinc compound, are blended with a cobalt compound. The following thing can be concluded from these knowledge.

[0062] That is, while the third components, such as zinc, have the plus operation made into the structure where cobalt cannot move the nickel cobalt solid-solution crystalline structure easily, they also have a minus operation of reducing the nickel hydroxide consistency of the solid solution and reducing the discharge capacity per unit active material weight. Therefore, it is thought that the over discharge property of A4 [A1 with more additions of the third component than A0 (0.5wt%) -] (2wt%) improved notably by A1 - A4 according to a plus operation of the third component although the minus operation of the third component appeared to some extent and the discharge capacity per unit active material weight fell slightly. Although it is necessary to make the loadings of the third component proper in order to demonstrate an operation of the third components, such as zinc, with sufficient convenience from this, the solid-solution internal transmigration of the cobalt compound at the time of over discharge can be effectively controlled according to a having-two-incomes operation with an operation of Co concentration gradient, without reducing most discharge capacity per unit active material weight, when the amounts of third components, such as a zinc compound, are made into 2% (metallic element weight % display).

[0063] [Processing conditions of a cobalt hydroxide enveloping layer] Alkali heat treatment was carried out on condition that the following to the coat solid-solution particle (BA0), and the conditions which can raise an electrochemical property further were examined.

[0064] (Alkali heat treatment conditions) Said coat active material particle BA 0 The coat active material particle [finishing / heat-treat in the heating air of each temperature for 3 hours;-and / alkali heat treatment / after carrying out impregnation of 25% of the weight of the sodium-hydroxide water solution] H-1, H-2, H-3, H-4, H-5, and H-6 It produced. Moreover, in order to investigate the class and effect of alkali, 25% of the weight of the hydroxylation KARIUMUMU

water solution was used instead of the above-mentioned sodium-hydroxide water solution, whenever [stoving temperature] was made into 80 degrees C, and the heat-treated [alkali] coat active material particle H-7 was produced for other conditions like the above.

[0065] Subsequently, each above-mentioned particle is used and it is a positive electrode EBA 0. While producing the positive electrode like the case, the electrochemical property was investigated by the same approach as the above. The result is shown in a table 5 with alkali heat treatment conditions.

[0066]

[A table 5]

	アルカリ熱処理条件		電気化学的特性値	
	アルカリの種類	加熱温度℃	単位活物質当たり放電容量	過放電指数
H-1	NaOH	30	101.0	99.1
H-2	NaOH	40	104.0	101.0
H-3	NaOH	60	107.1	103.0
H-4	NaOH	80	106.1	103.0
H-5	NaOH	100	104.0	101.0
H-6	NaOH	120	98.0	98.1
H-7	KOH	80	107.1	104.0

(被覆固体粒子BA₀を使用。前記電極EA₀を100 (基準) として表示)

[0067] the coat active material particle H-2 which carried out alkali heat treatment in a table 5, H-3, H-4, and H-5 -- the coat active material particle BA 0 (table 2 reference) of non-alkali heat treatment -- comparing -- both the discharge capacity per unit active material weight, and over discharge weighted solidity -- although -- it was improving. However, H-1 (heat treatment temperature of 30 degrees C) is BA0. The same weighted solidity was shown and the discharge capacity per unit active material weight was falling in H-6 (heat treatment temperature of 120 degrees C). When it is desirable to consider as 40 degrees C - 100 degrees C as for alkali heat treatment temperature and alkali heat treatment is performed to a coat active material particle on this condition from this, an electrochemical property increases notably.

[0068] On the other hand, H-7 which performed alkali heat treatment using the potassium-hydroxide water solution showed the electrochemical property which was further superior to H-2 to H-5. It is good to use a potassium hydroxide preferably as an alkali metal in alkali heat treatment from this.

[0069] In addition, it thinks to change to the high order cobalt compound more than divalent [the cobalt compound of an enveloping layer excels / divalent / in conductivity], and for an enveloping layer to change to the electrolytic solution and the description it is easy to get used to, and it is **** that an electrochemical property improves by alkali heat treatment.

Original document

POSITIVE ACTIVE MATERIAL FOR ALKALINE STORAGE BATTERY AND MANUFACTURE THEREOF

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Abstract of JP9082319

PROBLEM TO BE SOLVED: To enhance conductivity between active material particles with the small amount of cobalt compound by forming concentration gradient so that the concentration of the cobalt compound is high on the surface of a solid solution particle and gradually decreased toward the central part of the particle. **SOLUTION:** Nickel sulfate aqueous solution ((a) solution), zinc sulfate aqueous solution ((b) solution), and cobalt sulfate solution ((c) solution) are prepared so that the element weight fraction of zinc and that of cobalt are 0.5wt.% and 2wt.% respectively when the whole weight of solid solution particle is 100. The (a) solution and the (b) solution are mixed and stirred, and the (c) solution is added to the mixture so that the pouring amount per time is increased continuously or by stages. At the same time, ammonia water and sodium hydroxide aqueous solution are gradually added so that pH of (a), (b), and (c) solutions is kept in the specified value. Solid solution particle comprising compounds of nickel, zinc, and cobalt is obtained, and the cobalt compound is dispersed in the particle so as to have such concentration gradient that the concentration of the cobalt compound is low on the inside of the particle and high on the surface of the particle.

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